

ANALYTICAL ABSTRACTS

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Editor: NORMAN EVERS, B.Sc., Ph.D., F.R.I.C.
20, EASTCHEAP, LONDON, E.C.3
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Tetrabromophenolphthalein ethyl ester (potassium salt) is an indicator that has been put to a novel purpose. Its exceptionally great 'protein error' affords a method for the detection of proteins. See F. Feigl, *Spot Tests*, Vol. 2, p. 293. Elsevier Publishing Company (1954). The indicator has recently become available under H. & W. Code 8439.

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4-Methylnioxime is the latest reagent for nickel and palladium (see Banks & Hooker, *Anal. Chem.*, **28**, 79 (1956)). Nioxime itself has excellent sensitivity for nickel (1 in 10,000,000) but has its shortcomings as a gravimetric reagent. The newcomer is equally sensitive and can be used as a straightforward gravimetric reagent. It can be used in aqueous solution (about 0.3 per cent). Now listed by H. & W. under Code 5753.

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THE SOCIETY FOR ANALYTICAL CHEMISTRY

BULLETIN

CONGRESS ON MODERN ANALYTICAL CHEMISTRY IN
INDUSTRY, 1957

WE are living at present in the middle of a period of rapid technical developments in industry. One of the essential factors upon which these modern changes depend is analytical chemistry. Analysis plays a vital role in the manufacture of the chemical substances upon which so much of modern life and industry is now based. Most of the new plastics, many of the new drugs, modern paints and lacquers, synthetic textile fibres and many other objects of diverse sorts were unknown twenty years ago. Their production depends on complex manufacturing techniques. And these techniques would often be impossible without the new analytical procedures by which their manufacture is controlled.

A feature of modern analysis that represents almost a revolution in scientific thinking is the continuous supplementation of chemistry by physics. Increasingly, electronic equipment, spectrophotometers, polarographs, fluorimeters and other instruments depending on physical measurements automatically recorded are taking the place of the measurements and manipulations previously made by human operators. From this it is but a step to extend the design of the analytical instrument to control directly the industrial process, the sample of whose output it is examining.

The Society for Analytical Chemistry, through its Scottish Section, is organising a Congress to be held from June 24th to 28th, 1957, at St. Andrews University, at which these new developments in chemical analysis will be discussed and the possible directions of new advances in the future will be reviewed. Among subjects to be discussed are gas chromatography in the petroleum industry, new analytical methods in the electrical industry, the plastic industry, explosives, precious metals, foodstuffs and the pharmaceutical industry. There is to be a section on modern techniques and instrumentation covering automatic titration and the automatic recording of spectra in relation to industrial problems of analysis. Finally, the Congress aims to review the likely future developments in analytical chemistry, for example, the impact of new instruments, the relationship between official laboratories and chemists in industry, and the possibilities of geochemical prospecting—to name but three.

There will be an exhibition of some of the newer types of apparatus.

The organising committee of the Congress consists of Dr. Magnus Pyke, F.R.S.E., Mr. A. F. Williams, Mr. J. Brooks and Mr. H. C. Moir. The Congress Secretary is Mr. J. A. Eggleston, Divisional Analyst, Boots Pure Drug Co. Ltd., Airdrie Works, Airdrie, Lanarkshire, Scotland.

SYMPOSIUM ON MICROCHEMISTRY, 1958

It is proposed to hold a Symposium on Microchemistry in Birmingham over the period Wednesday, August 20th to Wednesday, August 27th, 1958 (both dates inclusive). This Symposium will be held under the auspices of the Society, and is being organised by the Midlands Section and the Microchemistry Group. Further details will be announced at a later date.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

XVth International Congress for Pure and Applied Chemistry, Paris, July 18th to 24th, 1957

THE XVth International Congress for Pure and Applied Chemistry will take place in Paris from July 18th to 24th, 1957, simultaneously with the XIXth Conference of the International Union of Pure and Applied Chemistry. It will be preceded by the Centenary Celebrations of the Société Chimique de France.

The Congress will be divided into three Sections, *viz.*: Physical Chemistry, Inorganic Chemistry and Organic Chemistry.

The papers intended for the various Sections should deal with one of the following subjects—

PHYSICAL CHEMISTRY—

- Physico-chemical aspects of radioactive elements;
- Combustion of gaseous mixtures;
- Water in chemical compounds;
- Diffusion in liquids and gels: reactions and structures.

INORGANIC CHEMISTRY—

- The solid compounds of transition metals (except complex compounds);
- The compounds of boron with hydrogen and non-metallic elements;
- Chemical properties of the elements in the actinium series;
- Chemical properties of substances at high temperature.

ORGANIC CHEMISTRY—

- Reaction mechanisms and intramolecular rearrangements;
- Organo-metallic and organo-metalloidal compounds;
- Selective reactions and orientation phenomena: stereochemistry;
- Structure and synthesis of natural compounds (except macromolecular substances).

An abstract of up to 250 words of any paper that authors in the United Kingdom and the Colonies wish to submit to this Congress should be sent to The British National Committee for Chemistry, The Royal Society, Burlington House, London, W.1, **not later than February 1st, 1957**. Authors in other countries should send their abstracts to their appropriate National Organisations. Congress members will not, as a rule, be requested to hand in the full texts of their papers.

The programme will include about fifteen main lectures.

Any language may be used for the lectures and papers, but it is preferable that a language be chosen that can be understood by the majority of the audience.

A general informative circular setting out the final organisation of the Congress will be sent out in the near future.

The address of the Congress is—

Secrétariat Général du XVIème Congrès International de Chimie pure et appliquée,
28, rue Saint-Dominique, Paris, 7e.

FORTHCOMING MEETINGS

Joint Meeting of the Scottish Section with the Methods of Analysis Panel (Glasgow), September 28th, 1956

A JOINT Meeting of the Scottish Section and the Methods of Analysis Panel (Glasgow) will be held at 7.15 p.m. on Friday, September 28th, 1956, at the Central Station Hotel, **Glasgow**.

The following papers will be presented and discussed—

"The Analysis of Titanium and its Alloys," by W. T. Elwell, F.R.I.C.

"The Estimation of Molybdenum," by R. Kerr, B.Sc., A.R.I.C.

Ordinary Meeting of the Midlands Section, September 11th, 1956

AN Ordinary Meeting of the Section will be held at 7 p.m. on Tuesday, September 11th, 1956, at the University, Edmund Street, **Birmingham, 3.**

A lecture on "Recent Advances in the Analysis of Cast Iron and Foundry Materials" will be given by W. E. Clarke.

Ordinary Meeting of the Midlands Section, September 27th, 1956

AN Ordinary Meeting of the Section will be held at 7.15 p.m. on Thursday, September 27th, 1956, at the College of Art, **Derby.**

A lecture on "High-precision Absorptiometry" will be given by W. T. L. Neal.

COMMUNICATIONS ACCEPTED FOR PUBLICATION IN *THE ANALYST*

THE following communications have been accepted for publication in *The Analyst*, and are expected to appear in the near future. It is not possible for the Editor to enter into correspondence about any of them.

"Determination of Copper in Steel," by L. J. A. Haywood and P. Sutcliffe.

"A Specific Test for Cobalt," by F. Feigl and D. Goldstein, *translated* by R. E. Oesper.

"Studies on Hypovanadous Salts as Analytical Reagents," by C. M. Ellis and A. I. Vogel.

"Contamination During the Micro-determination of Magnesium with 8-Hydroxyquinoline," by E. J. Butler and A. C. Field. (Note.)

"The Investigation of Various Chemical Systems by Electron-spin Resonance," by D. J. E. Ingram.

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

2380. Review of fundamental developments in analysis. *Anal. Chem.*, 1956, **28** (4), Part II.—This review includes the following contributions. **Light-absorption spectrometry**, M. G. Mellon and D. F. Boltz (559-576). **Infra-red spectroscopy**, R. C. Gore (577-578). **Ultra-violet spectrophotometry**, R. C. Hirt (579-583). **X-ray absorption and emission**, H. A. Liebhaufsky and E. H. Winslow (583-591). **X-ray diffraction**, B. Post and I. Fankuchen (591-595). **Raman spectroscopy**, E. J. Rosenbaum (596-597). **Electron microscopy**, M. Swerdlow, A. J. Dalton and L. S. Birks (597-609). **Mass spectrometry**, V. H. Dibeler (610-615). **Emission spectroscopy**, W. F. Meggers (616-621). **Fluorimetric analysis**, C. E. White (621-625). **Polarographic theory, instrumentation and methodology**, D. N. Hume (625-637). **Organic polarography**, S. Wawzonek (638-649). **Instrumentation**, R. H. Müller (649-660). **Electro-analysis**, D. D. DeFord (660-666). **Amperometric titrations**, H. A. Laitinen (666-671). **Potentiometric titrations**, C. N. Reilley (671-678). **Acid-base titrations in non-aqueous solvents**, J. A. Riddick (679-687). **Chromatography and electrochromatography**, H. H. Strain and T. R. Sato (687-694). **Inorganic gravimetric and volumetric analysis**, F. E. Beamish and A. D. Westland (694-705). **Volumetric and gravimetric analytical methods for organic compounds**, W. T. Smith, jun., W. F. Wagner and J. M. Patterson (706-714). **Biochemical analysis**, E. L. Duggan (714-720). **Distillation analysis**, A. Rose and J. Acciarri (720-723). **Extraction**, L. C. Craig (723-729). **Ion exchange**, R. Kunin, F. X. McGarvey and A. Farren (729-736). **Nucleonics**, W. W. Meinke (736-756). **Inorganic microchemistry**, P. W. West (757-766). **Organic microchemistry**, C. L. Ogg (766-769). **Statistical methods in chemistry**, J. Mandel and F. J. Linnig (770-777). **Characterisation of organic compounds**, C. W. Gould (777-782). J. R.

2381. Analysis for industry: new reagents for colorimetric analysis. W. I. Stephen. *Ind. Chem. Mfr.*, 1955, **31**, 622-624; 1956, **32**, 38-40.—The use of a considerable range of new organic reagents for the colorimetric determination of Mo, U, Ti, Zr, Ca, Cu, Fe, Th, Ba, Zn and V is reviewed. (41 references.) S.C.I. ABSTR.

2382. Complex compounds of copper with amines and their use in the detection of certain anions. A. P. Kreshkov and K. I. Filippova. *Trudy Moskov. Khim.-Tekhnol. Inst. im. D. I. Mendeleeva*, 1954, (18), 61-66; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,090.—Complex cations of Cu with organic addends—benzidine, o-tolidine, aniline, o-toluidine, p-toluidine and amidopyrine—are applied to the detection of $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, SCN^- and I^- . The copper-benzidine complex can be used also for the identification of thiourea. G. S. SMITH

2383. Drop method of determination of elements from the limiting dilution of solutions. G. G. Kobayak. *Uch. Zap. Molotov. Univ.*, 1954, **8** (3), 21-27; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,085.—A capillary is marked at three points. The top mark is that to which a liquid rises under capillary forces, the middle mark is at half of this height and the bottom mark is at a quarter of it. In use, two coloured spots are obtained on filter-paper by using volumes of soln. corresponding to the top or the middle mark, and to the bottom mark. The soln. is so diluted that when the middle mark is used it is possible to determine with certainty the minimum amount detectable of a substance in soln., and when the bottom mark is used the result should be inconclusive, sometimes positive and sometimes negative. Good reproducibilities for the limiting dilution figure are obtainable. For the determination of an element, standard soln. are first used to obtain the limiting dilution; then, from a knowledge of the concn. at the limiting dilution and the amount of solvent added to the known vol. of the sample soln., the concn. of the element can be determined. The sensitivity of the reaction depends on the type of paper, the pH of the medium and the colour intensity of the reaction products. The standard and the sample soln. must be similar in acidity and in the concn. of other salts. Lead and Cu in soln. of their salts, and Cu in oxidised copper ores can be determined in this way. The method is more accurate than that of spot colorimetry. It is applicable to field conditions in geological exploration. G. S. SMITH

2384. Studies on the redox indicator phenoxazone. I. Soichiro Musha and Toyokichi Kitagawa (Fac. Eng., Naniwa Univ., Sakai, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (11), 1289-1291.—The reddish colour (max. absorption, 460 m μ) of phenoxazone (I) changes to blue on the addition of a reducing agent (redox potential, 0.35 V vs. the N.H.E.). The change is so marked and both colours are so stable that I can be used as an indicator for a redox titration involving a strong reducing agent. Its use (0.25 per cent. in N HCl) for the reaction between Fe^{3+} and Sn^{2+} was studied and it was found that Cr^{3+} , Cu^{2+} , Ti^{3+} and V^{3+} interfere. For a quick response of the indicator the presence of Cl^- is advantageous. K. SAITO

2385. The use of Metanil yellow, Astral blue, Xylene blue and Setoglaurin in cerimetry. J. Bognár and Z. Nádler (Rákosi Mátyás Polytech. Univ. Heavy Industries, Miskolc, Hungary). *Magyar Kém. Foly.*, 1955, **61** (11), 372-376.—The use of Metanil yellow (I) [4-(3-sulphobenzenazo)diphenylamine, sodium salt] and Astral blue G (II) (an ethyl or ethoxy derivative of triaminotriphenylmethane) in cerimetric titrations is described. II has a colour change at +0.72 V (vs. the S.C.E.), which is about equal to the equiv. potential of the Fe^{3+} -ceric sulphate reaction. II can be used in the cerimetric determination of

Fe^{II} (also in the presence of HgCl_2 and HgCl_4), ferrocyanide, As, Ti and quinol. In addition to these, **I** can be used for the titration of Mo^V , U and ascorbic acid. Tervalent Sb can be titrated in conc. HCl soln., in the presence of **I**, but As needs ICl as catalyst and thus their mixture can be determined. The colour change of **I**, which was used, is irreversible (carmine red to greenish blue); the colour change of **I** in its oxidised form is reversible, but less intense and less contrasting. Neither indicator can be used for the cerimetric titration of I , H_2O_2 , Ta, NO_2^+ , V^{IV} and oxalate, with any of the procedures attempted. Xylene blue VS and Setoglaurin O behave similarly to **II**. A. G. PETO

2386. Compleximetric micro-titrations using PAN [1-(2-pyridylazo)-2-naphthol] as indicator. H. Flaschka and H. Abdine (Nat. Res. Council, Dokki, Cairo, Egypt). *Chemist Analyst*, 1956, **45** (1), 2-3.—Difficulties have been encountered in the use of 1-(2-pyridylazo)-2-naphthol (**I**) as an indicator in compleximetric titrations of Cu and Zn, since the indicator and its complexes are sol. only in organic solvents, and since the complexes are of the same order of stability as those formed by the titrant. The difficulties are largely overcome by employing a back-titration, and in this way Fe, Cu, Ni, Co, Zn, Cd, Pb, Ga and any metal whose complex with EDTA has a stability constant $> 1 \times 10^{10}$ are determined by titrating an excess of EDTA with Cu^{++} soln. There is no interference from Ca and Mg, nor from small amounts of Mn, but Al must be absent. If these determinations are carried out in acid soln. then, on making the soln. ammoniacal, Ca, Mg and Mn can be estimated by titrating with EDTA, with **I** as indicator. The titration errors for 0.01 M soln. are ± 0.03 ml, and can be reduced by taking the average of three or four end-points. J. H. WATON

2387. Electrometric titrations. A. Anastasi, U. Gallo, E. Mecarelli and (the late) L. Novacic (Control Lab., Farmitalia, Viale Bezzi, Milan, Italy). *J. Pharm. Pharmacol.*, 1956, **8** (4), 241-255.—Recent advances in the application of electrometric methods in pharmaceutical analysis are surveyed under the following headings—potentiometry, including the dead-stop end-point; titrations in non-aqueous media; conductimetry; polarography, including oscillographic polarography; amperometry; coulometry; and high-frequency titrations. (206 references.) A. R. ROGERS

2388. A fundamental research on high-frequency titration. (The effect of shielding the solution.) Kunio Nakano (Faculty of Sci., Rikkyo Univ., Ikebukuro, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (10), 1096-1101.—The peak on the resistance-concn. curve of high-frequency titrations (coil and condenser types) (*cf. Anal. Abstr.*, 1955, **2**, 1731) is eliminated when the container of the sample soln. is shielded with a metal film. This has been theoretically discussed with the aid of equiv. circuits. When a dil. soln. (0.0001 to 0.01 M) of an electrolyte, having a higher resistance than metal, is used as a shield, the concn. at which the peak is observed and the peak resistance are changed according to the concn. of the electrolyte. The higher the frequency and the larger the inductance, the more marked is the extent to which the curve is shifted. Partial shielding with the aid of an electrolyte of a suitable concn. can increase

the accuracy of high-frequency titrations of condenser type through the elimination of the peak point, which is unfavourable for an accurate titration. K. SAITO

2389. Theory and technique of paper chromatography. II. J. Moreno Calvo (Centro Exper. del Frio, Spain). *Rev. Cienc. Apl.*, 1955, **9**, 510-523.—The technique of paper chromatography is discussed, particularly choice of developing solvent, ascending, descending and circular procedures, apparatus, quantitative applications, and paper electrophoresis. L. A. O'NEILL

2390. Studies on paper-chromatography. I. Factors affecting R_F and S values with impregnated filter-papers. A. C. Chatterji and H. Bhagwan (Lucknow Univ., India). *Z. anal. Chem.*, 1956, **149** (5), 339-345.—Factors affecting the chromatographic separation of Pb^{II} , Ag^I and Hg^I on filter-paper strips impregnated with KI and K_2CrO_4 are studied. The diffusing solvent is 60 per cent. aq. alcohol, and agar, starch, or dextrin the protecting colloid. It is shown that R_F and S values can be controlled by altering the concn. of the KI and K_2CrO_4 and of the colloid in the impregnating soln. The S value is the "spreading factor" and is defined as the ratio of the final band width to the initial band width (Laskowski and McCrone, *Anal. Chem.*, 1951, **23**, 1579). J. P. STERN

2391. The role of the acid concentration of the solvent in inorganic paper-chromatography. Conditions for the formation of a compact spot. G. Almásy and I. Dezső (Phys. Res. Inst. Hung. Acad. Sci., Debrecen, Hungary). *Magyar Kém. Foly.*, 1956, **62** (2), 60-64.—The dependence of the movement of many metal ions on the acid (and water) content of various water-miscible solvents (alcohol-water-conc. HCl) was examined, with 50 μg of metal and the ascending method. It was found that the length of the spot decreases with increasing acid concentration. Increasing the water content of the solvent causes the length of the spot either to increase initially, or it remains unchanged and then decreases in every case. Anhydrous solvents are not suitable for the separation of metal ions, because it was found that when an ethanolic anhydrous solvent was used the spots due to Fe^{+++} broke up into several spots. A similar result was obtained when a water-containing solvent was used and the paper was saturated with the vapour of the anhydrous solvent. A. G. PETO

2392. Gas-liquid chromatography. A. T. James (Nat. Inst. Medical Research, London). *J. Pharm. Pharmacol.*, 1956, **8** (4), 232-240.—The procedure for the separation and identification of volatile materials by gas-liquid chromatography is briefly described. The vapours may be detected in the gases emerging from the column by titration, by measurement of thermal conductivity, or by the gas density meter of Martin and James (*Biochem. J.*, 1956, **63**, 144). The factors influencing the separation are discussed. A. R. ROGERS

2393. Laboratory applications of ion-exchange resins. I. P. Morris and R. E. Stuckey (Brit. Drug Houses, London). *Lab. Practice*, 1956, **5** (3), 92-97.—This is a general introduction dealing with the various types of resins used and the basic principles of ion-exchange technique. Special

applications, such as the determination of salts, analysis of insoluble substances, and separation of similar ions by ion-exchange chromatography, and of amino acids in protein hydrolysates, are described.

H. A. FISHER

2394. Selectivity and specificity of ion exchangers. R. Griessbach (VEB-Farbenfabriken, Wolfen, Kr. Bitterfeld, Germany). *Angew. Chem.*, 1955, **67** (19-20), 606-613.—The exchange of ions of the same and different valencies is considered theoretically, and equations are developed involving the selectivity quotient (coefficient). Specificity of the ion-exchange resins is considered in terms of ion-pair formation, polarisation, acid or base strengths of the resin groups, rate of working, pre-treatment of the resin or the ions to be exchanged, and molecular-sieve action.

J. H. WATON

2395. Ion exchange in a mixture of acetone and water with cation exchangers. Hidetake Kakihana and Kenji Sekiguchi (Pharmacy of Tokyo Univ. Hospital, Hongo, Tokyo). *J. Pharm. Soc. Japan*, 1955, **75** (1), 111-113.—The influence of increasing amounts of acetone on the exchange between sodium and hydrogen ions was studied with the cation exchangers Dowex 50 X-1, X-2, X-4, X-8 and X-16. The equilibrium constants were measured by passing through a mixture of water and acetone (0 to 60 per cent.) containing 0.05 N NaCl and 0.05 N HCl and titrating the H⁺ in the eluate. The selectivity of Na⁺ increases with the acetone content, the reciprocal of the log. of the equilibrium constant being roughly proportional to the dielectric constant of the mixture. K. SAITO

2396. Precision of extinction measurements in a spectrophotometer of the compensation type. M. J. Maurice ('Research', AKU, Arnhem, Holland). *Chem. Weekbl.*, 1956, **52** (6), 93-97.—The following causes for variations in the accuracy of measurements in compensating spectrophotometers are given—fluctuation in photocell response and voltage of battery supplying compensating current, fluctuation in dark current, and inaccuracy in establishing zero and in measuring transmission intensity. Formulae defining each contributing factor are given and an overall formula giving the total error is established. The following simplified expression is finally arrived at: $\text{Var}(E) = P + Q \cdot 10^{2B}$, where P represents influences inherent in the equipment, and $Q \cdot 10^{2B}$ factors derived from manipulation. Experimental determinations of P and Q , with a Unicam SP 600 spectrophotometer, establish that values for P are negligible. Closer examination of Q shows that, of the manipulations required for extinction measurement, compensation contributes most towards variation of extinction measurements, and transmission readings least.

H. A. FISHER

2397. Total porosity and particle density of fluid catalysts by liquid titration. W. B. Innes (American Cyanamid Co., Stamford, Conn., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 332-334.—The total porosity of absorbents and catalysts is obtained titrimetrically by measuring the amount of liquid required to cause the sample to cake and consequently to adhere to the sides and bottom of the vessel. Water is an ideal liquid for porous inorganic material that does not undergo swelling on contact with water. *Procedure*—The sample (25 g) is transferred to a 4-oz screw-top bottle, and an amount of water less than the expected pore vol. is allowed to run

in rapidly. The bottle is shaken vigorously for ≈ 20 sec., and is cooled under the tap. Any lumps are broken up with a spatula. Water is further added in 0.2-ml increments, the bottle being shaken for ≈ 15 sec. and any lumps broken up between additions. The end-point is reached when the powder does not flow freely on up-ending the bottle, the material sticking to the bottom for 2 sec. or more. Most material reaches equilibration within 15 min., but for exact results complete equilibration requires 20 hr. The results are comparable with those obtained by nitrogen desorption where macroporosity is negligible. Some equilibrium and hydroformer catalysts have titration pore vol. in excess of the nitrogen values, indicating small macroporosity. It is not recommended that the particle density be evaluated from the pore vol. and the skeletal density. After measurement of the pore vol., the sample is made into a slurry, diluted to 100 ml in a pycnometer, and the particle and skeletal densities are determined independently.

J. H. WATON

2.—INORGANIC ANALYSIS

2398. Inorganic paper-chromatography. XXIII. Chromatographic behaviour of various cations and their counter anions. Shirō Harasawa and Takashi Sakamoto (Fac. Eng., Yamaguchi Univ., Ube, Yamaguchi Prefecture). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (11), 1322-1324.—The chromatographic behaviour of cations and anions of a salt was studied with developers containing various electrolytes, including HCl, H₂SO₄, HNO₃, acetic acid, aq. NH₃ soln. and pyridine. When salts are developed with org. solvents without an electrolyte, only those that have a molecular nature, e.g., HgCl₂, migrate, others remain at the initial spot. When solvents containing NH₃ or acetic acid are used as developers, hydrolysis takes place to produce less ionic species, such as hydroxides or ammine complexes, two bands due to the anionic and cationic components being formed. When mineral acids are used, metal ions move behind the front of H⁺, two bands being formed, as with acetic acid or ammonia.

K. SAITO

2399. Precipitation chromatography of cations on filter-paper with 8-hydroxyquinoline. I. Detection of copper, ferric, cobaltous and nickel ions. Hideo Nagai (Fac. Sci., Kumamoto Univ., Kumamoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (11), 1246-1248.—Filter-paper is impregnated with an ethanolic soln. of 8-hydroxyquinoline (1.5 per cent. in 95 per cent. ethanol) and a slit 1 to 2 mm long is made in the centre of the sheet. The sample soln. containing Cu, Fe⁺⁺⁺, Co and Ni is spotted on the slit, which is penetrated at right angles by a thin (1 mm wide) strip of filter-paper. One end of this strip is dipped in the developer and the spot is horizontally developed in a sealed vessel. For the separation of the spots of these ions, a saturated aq. soln. of butanol is the best developer. The spots spread in the sequence Cu (yellowish green), Fe (black), Ni (light green) and Co (yellow) (from inside to outside). The new method decreases the time taken for the development (< 1 hr.).

K. SAITO

2400. Volumetric studies in oxidation-reduction reactions. VII. Reduction with ferrous ethylenediamine sulphate: ceric sulphate method. Balwant Singh and Sarwan Singh (Panjab Univ. Coll.,

Hoshiarpur, India). *Anal. Chim. Acta*, 1956, **14** (3), 213-216.—Ferrous ethylenediamine sulphate (I) can be used as a reducing agent in acid soln. for the accurate volumetric determination of KClO_3 , KBrO_3 , KIO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{K}_3\text{Fe}(\text{CN})_6$, KMnO_4 , $\text{K}_2\text{S}_2\text{O}_8$, H_2O_2 and $\text{Ce}(\text{SO}_4)_2$. An excess of I (0.05 N) is added to a soln. of the sample, the acidity of the mixture is adjusted to between 1 and 2 N (4 and 6 N for KClO_3 and KBrO_3), and the excess of I is then titrated with 0.05 N $\text{Ce}(\text{SO}_4)_2$ soln., ferroin being used as indicator. W. J. BAKER

2401. Amperometric titration of two- and three-component mixtures of metal ions with EDTA. C. N. Reiley, W. G. Scribner and C. Temple (Univ. of North Carolina, Chapel Hill, N.C., U.S.A.). *Anal. Chem.*, 1956, **28** (4), 450-454.—The successive amperometric titration of each metal in mixtures of Bi, Pb and Ca, Fe and Mn, or Cu and Ca can be effected, with an error of < 1 per cent., by the combined use of the cathodic diffusion current of the metal ions and the anodic diffusion current of EDTA (disodium salt) at controlled pH and potential. Thus Bi^{3+} form a stable complex with EDTA at pH 2, while Ca^{2+} and Pb^{2+} do not, but Pb^{2+} complex strongly at pH 4 although Ca^{2+} do not, so that the titration can be made by changing the pH after each end-point. The first two end-points are observed cathodically, and the end-point for Ca at pH 8 by the appearance of the anodic diffusion current of the excess EDTA. The measurements are made at -0.25, -0.55 and +0.05 V vs. the S.C.E., for Bi, Pb and Ca, respectively, and both oxygen and Cl^- should be rigorously excluded from the soln. Data for the stability of 15 metal ions with EDTA at pH 2, 4 and 9.1 indicate the possible titration of each metal in certain conditions; the potentials at which current measurements are made can be calculated from characteristic polarograms. Addition of gelatin (0.005 to 0.033 per cent.) is sometimes necessary for the selective elimination of interfering polarographic waves. Two new polarographic methods for determining stability const. are described and their limitations discussed. W. J. BAKER

2402. Coulometric titrations with electrically released EDTA. Titrations of calcium, copper, zinc and lead. C. N. Reiley and W. W. Porterfield (Univ. of North Carolina, Chapel Hill, N.C., U.S.A.). *Anal. Chem.*, 1956, **28** (4), 443-447.—A coulometric titration cell and procedure for the determination of milligram amounts of Ca^{2+} , Cu^{2+} , Zn^{2+} and Pb^{2+} with EDTA (indirectly generated by electro-reduction of 0.02 to 0.03 M mercuric ethylenediaminetetra-acetate complex at a mercury pool) are described. The titration is made with const. current at pH 8.5, a mercury drop being used for end-point detection; EDTA is generated with 100 per cent. current efficiency. Oxygen must be rigorously excluded from the cell. A potential-pH graph for the equilibria is shown, and is combined with polarograms for the kinetic effects to determine the most suitable operating conditions. These are discussed fully. The error is normally < ± 1 per cent. The method can be extended to other metal ions. W. J. BAKER

2403. Compleximetric titrations in more strongly acidic medium. Back-titration with bismuth nitrate against catechol violet. H. Flaschka and F. Sadek (Nat. Res. Council, Dokki, Cairo, Egypt). *Z. anal. Chem.*, 1956, **149** (5), 345-355.—Conditions for the compleximetric back-titration of various metal-ion mixtures are discussed, with special reference to

the behaviour of Cu, Ni, Al, Co, Cr, Zr, Hg, Fe, In, Ga and Th on being back-titrated with Bi at pH 2 to 3. Interference, especially by Cu, Ni and Al, is due to the very slow reaction of the complexes of these metals. Interference of Hg is suppressed by NaCl and of SO_4^{2-} by addition of $\text{Ba}(\text{NO}_3)_2$. The method is used for the determination of In, Ga, Fe and Th and gives high accuracy. **Procedure**—To the sample soln. add the calc. excess of 0.01 M EDTA (disodium salt) and adjust the pH to between 2 and 3. Add 2 to 3 drops of 0.1 per cent. aq. catechol violet and dilute to a vol. of 80 to 100 ml. Titrate with 0.01 M $\text{Bi}(\text{NO}_3)_3$ in 0.5 to 1.0 N HNO_3 to a blue colour and determine the exact end-point (yellow) by successive small additions of EDTA and bismuth soln. J. P. STERN

2404. Reaction of hydrogen peroxide with complexes of ethylenediaminetetra-acetic acid and nitrilotriacetic acid. Kuang Lu Cheng and P. F. Lott (Univ. of Connecticut, Storrs, Conn., U.S.A.). *Anal. Chem.*, 1956, **28** (4), 462-465.—New colour reactions of Fe, Co and other common metals with EDTA (0.1 M) and nitrilotriacetic acid (I) (0.25 M) in the presence of H_2O_2 at pH > 10 are reported. The complex Fe - EDTA gives a purple colour, Fe - I an unstable brown colour, whilst Co - EDTA gives a blue colour and Co - I a purple colour. The possible application of these coloured peroxy complexes (which follow Beer's law) in the quantitative analysis of solutions containing Fe, Co, EDTA or I is discussed. A simple, selective procedure for the spectrophotometric determination of U (3 mg per 25 ml of soln.) in the presence of Fe, Mo, V, Cr or Co, with a mixture of I, H_2O_2 and aq. NH_3 , is described. The measurements are made at 445 m μ if the contents of Fe, Cr and Co are < 0.5 (as FeCl_3) or 4.5 (as FeSO_4), 0.5 and 3.5 mg per 25 ml, respectively, and at higher wavelengths if larger amounts of V, Mo and W are present. This yellow peroxy complex of U with I can also be used as a simple field test in prospecting for U.

W. J. BAKER

2405. Chelating agents in non-aqueous titrimetry. B. D. Brummet and R. M. Hollweg (T. A. Edison, Inc., West Orange, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (4), 448-450.—Either Ni^{2+} , Cu^{2+} or Co^{2+} in aq. soln. (0.1 to 0.2 M) can be determined by evaporating the soln. to dryness and dissolving the residue in methanol (5 ml); an excess of a suitable chelating agent is added, followed by 20 ml of benzene, and the soln. is then titrated potentiometrically with 0.1 N NaOH in methanol-benzene (1 + 4). Very sharp inflections at the equivalence points are obtained with dimethylglyoxime (I), dithizone (II), 8-hydroxyquinoline (III) and 1-nitroso-2-naphthol (IV). Any one of these can be used for the titration for Ni, but only II and IV are suitable for Co, and only I and III for Cu. The extended use of non-aqueous solvents for chelate titrimetry is discussed. W. J. BAKER

2406. Determination of low concentrations of moisture in gases by a psychrometric method. R. N. Rubinshtein and N. A. Glukhareva. *Zavod. Lab.*, 1956, **22** (1), 66-70.—Low concn. of moisture in gases are measured by means of a psychrometer in which water is replaced by H_2SO_4 . The method is accurate to within ± 0.2 mg of H_2O per litre.

G. S. SMITH

2407. Determination of "water-soluble alkali" in cement. O. A. Ellingson, J. L. Gillam and J. E. Kopanda (Universal Atlas Cement Co., Gary, Ind., U.S.A.). *Bull. A.S.T.M.*, 1956, No. 212, 63-66.—

A study of five variations of the A.S.T.M. method (C 114-53) for determining "water-sol. alkali" in cements resulted in the following preferred procedure. A slurry of cement (25 g) and H_2O (250 ml) is shaken for 10 min. at room temp., filtered on a Büchner funnel, and the concn. of Na_2O and K_2O in the filtrate is then determined by flame photometry. The measurements are made on 50 ml of the filtrate acidified with conc. HCl (5 ml) to which are added 8.5 ml of standard aq. $CaCl_2$ (prepared according to method C 228-49T) and the soln. is made up to 100 ml. The results are expressed as per cent. Na_2O as calculated from (per cent. $K_2O \times 0.807$) + per cent. Na_2O .

W. J. BAKER

2408. A spectrographic method for the determination of sodium in aluminosilicate catalysts. D. Zulfugary and V. Zizin. *Nov. Neft. Tekn. Neftepererabotki*, 1954, (2), 9-11; *Ref. Zhur., Khim.*, 1955, (15), Abstr. No. 31,856.—For the determination of 0.1 to 1 per cent. of Na in aluminosilicate catalysts, the intensity of the Na doublet $\lambda = 3302$ and 3303 in relation to the background is used. Standard samples, prepared from the raw material with known amounts of Na, are heated at $750^\circ C$ for 3 hr. The standards and the samples are placed on four-cornered electrodes (40 mm long, 6 mm in diameter) and sparked with a 15-sec. exposure each (total exposure 1 min.). The upper electrode is sharpened to a cone with a curved top; in the lower is drilled a pit 2 mm in diameter and depth. The state of division and dryness of the samples influence the combustion of the sample. To construct a calibration curve, five standards are sparked.

C. D. KOPKIN

2409. Syntheses and uses of new analytical reagents for potassium. III. "Thiohexyl." Kyoji Tōei (Dept. of Chem., Faculty of Sci., Okayama Univ., Japan). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, 76 (10), 1083-1085.—"Thiohexyl" (tetranitrophenothiazine-9-oxide) (I) prepared by Kehrman's method (*Ber.*, 1913, 46, 3018) was dissolved in Li_2CO_3 (8.5 g in 1 litre of 1 per cent. Li_2CO_3) and its reaction with K was studied. Red, fine crystals of the potassium salt of I are obtained by the addition of I (in amount greater than twice the equiv. of the K) to a neutral or weakly basic soln. of K (>0.2 g per litre). When the liquid is heated to boiling point and set aside for > 12 hr. the ppt. is converted into purple, prismatic crystals, which can be dried ($110^\circ C$) and accurately weighed. Both Na and Mg interfere and cannot be masked with tartrate or EDTA.

IV. Tetranitroacidone. *Ibid.*, 1955, 76, 10, 1085-1088.—Tetranitroacidone (II) was synthesised by Bader's method (*Annalen*, 1907, 355, 327) and its use for the gravimetric analysis of K was studied. The sample soln. is neutralised with Li_2CO_3 , treated with II soln. (0.5 per cent. in 1 per cent. Li_2CO_3) at the boiling point and set aside overnight. The red ppt. is collected on a sintered-glass filter, washed with a saturated soln. of K-II (in 0.4 per cent. Li_2CO_3 , 3 ml) and several drops of water and dried at $110^\circ C$. Interference is caused by Na and Mg.

K. SAITO

2410. Determination of potassium by precipitation and titration of its tetraphenylboron salt: use of a simple filtration assembly. H. W. Berkhout and G. H. Jongen (State Agric. Test and Res. Sta., Maastricht, Holland). *Chemist Analyst*, 1956, 45 (1), 6-7.—The pptn. of K with Na tetraphenylboron is carried out in the presence of formaldehyde and alkali to prevent interference from ammonium

salts, and with the addition of EDTA to keep calcium and magnesium salts in soln. After filtration in a filter-tube packed with glass wool, sintered at red heat, and Hyflo-Supercel as a filter aid, the ppt. is dissolved in acetone and the estimation is completed argentimetrically, with K_2CrO_4 as indicator. As little as 0.5 mg of K_2O may be estimated.

J. H. WATON

2411. Titrimetric determination of potassium via tetraphenylboron precipitation and cationic resin exchange. H. Flaschka and F. Sadek (Nat. Res. Council, Dokki, Cairo, Egypt). *Chemist Analyst*, 1956, 45 (1), 20-21.—In the simple method described, the ppt. of K tetraphenylboron is dissolved in acetone and allowed to run through a strongly acid ion-exchange resin. The free tetraphenylboron acid is sufficiently stable to be titrated within 10 min. Procedure—The soln. of sample, containing <10 mg of K, is neutralised with NaOH or HCl , and is diluted to ≈ 50 ml. After the addition of 0.5 ml of conc. HCl and 10 ml of Na tetraphenylboron soln. (1.2 per cent.), the soln. is well stirred and allowed to stand for at least 5 min. The ppt. is separated with a porcelain filter-stick, washed with 3-ml portions of dil. Na tetraphenylboron reagent (1:9) and finally twice with 1-ml portions of H_2O . The ppt. is dissolved in acetone, transferred to the original pptn. vessel, and an equal vol. of H_2O is added. Any turbidity is removed by the addition of a little acetone. The soln. is transferred to an exchange column containing a strongly acidic type of resin (e.g., Zeo-Karb 225). The beaker is rinsed with a little acetone-water mixture, and the column is washed with this soln. and then with several 5-ml portions of water until the eluate is neutral. The mixed eluates are titrated immediately with 0.01 N NaOH soln., with a methyl red-methylene blue indicator (equal vol. of 1 per cent. soln. of each indicator, freshly mixed), until the soln. is a clear stable green. The titration soln. readily absorbs CO_2 , which cannot be expelled without accelerating the decomposition of the tetraphenylboron acid. However, satisfactory results are obtained with the above-mentioned mixed indicator by titrating to a permanent green instead of the usual grey colour. The results are comparable in accuracy with those obtained by other titrimetric methods, being in general correct to within 1 to 2 drops of alkali (≈ 10 to $30 \mu g$ of K).

J. H. WATON

2412. Radiometric determination of potassium. I. M. Korenman and E. I. Zorin (Inst. Chem., Gorki State Univ.). *Zavod. Lab.*, 1955, 21 (12), 1419-1421.—With a special cell the measured activity of the natural radioactive isotope ^{40}K is raised to 33 impulses per min. per 1 per cent. of K_2O . A method of determining K in various salts and mixtures not containing other radioactive elements is described.

G. S. SMITH

2413. A method of analysis of technical cuprous oxide. T. F. Makarova and M. I. Erokhina. *Byull. Osmeny Opytom. Lakokras Prom.*, 1954, (6), 50-53; *Ref. Zhur., Khim.*, 1955, (15), Abstr. No. 31,927.—To extract Cu_2O , add to the sample (0.3 to 0.5 g) 30 to 40 ml of N NH_4Cl and 5 to 10 ml of 25 per cent. aq. NH_3 , warm, filter off Cu and CuO , wash the ppt. with water, and dilute the filtrate and washings to 250 ml. Heat a 25-ml aliquot till no more NH_3 can be smelt, cool, acidify with 25 per cent. H_2SO_4 (2 ml), add 2 g of KI, and titrate the liberated I with 0.1 N $Na_2S_2O_3$. To determine metallic Cu, treat the filter-paper and ppt. in a

beaker with a soln. of FeCl_3 in HCl (75 g of FeCl_3 and 150 ml of conc. HCl), add 500 ml of water, and warm to dissolve the Cu. Filter off insol. CuO , wash the ppt. with hot water, and titrate the filtrate with 0.1 *N* KMnO_4 in the presence of 5 ml of conc. H_3PO_4 to a permanent pink. Warm the filter-paper and CuO with HNO_3 (1:2), filter into a porcelain dish, add 2 ml of conc. H_2SO_4 , and evaporate to fumes of SO_3 ; cool, add 10 to 15 ml of water, and once more evaporate to copious fumes of SO_3 . To the cooled soln. add 2 g of KI , and titrate the I with 0.1 *N* $\text{Na}_2\text{S}_2\text{O}_3$ from a micro-burette.

C. D. KOPKIN

2414. Chelatometry. VI. Determination of higher cupric-ion concentrations with EDTA. P. Wehber (Metallhütte Mark A.-G., Hamburg-Wilhelmsburg, Germany). *Z. anal. Chem.*, 1956, **149** (4), 244-249.—The use of Variamine blue B (4-amino-4'-methoxydiphenylamine) indicator (*cf.* Erdey and Bodor, *Brit. Abstr. C*, 1953, 332) makes possible the chelatometric determination of 3 to 30 mg of Cu with EDTA in the presence of SCN' and of Na acetate. Larger amounts of Cu (< 150 mg) may be determined by trial titration and subsequent accurate titration, during which SCN' are added near the pre-determined end-point. Accuracy is well within ± 0.2 mg. The possibility of replacing SCN' (which may interfere) by Cl' or by hexamine-HCl buffer (pH 5.5) is discussed, but generally low results are obtained by these modifications. *Procedure*—Buffer the weakly acidic CuCl_2 soln. with 3 to 5 g of Na acetate (pH ≈ 5.5 but > 6). Add the indicator (60 to 80 mg of NaCl containing 1 per cent. of Variamine blue B) and NH_4SCN (1 to 2 g) and immediately titrate at $< 20^\circ\text{C}$ with 0.1 *M* EDTA until the blue-violet colour changes to blue-green; after 1 min. complete the titration if necessary.

J. P. STERN

2415. Amperometric titration of copper with anthranilic acid. A. K. Zhdanov and R. I. Tseitlin. *Trudy Sredneazial. Gosudarst. Univ. (Tashkent)*, *Khim. Nauk.*, 1954, **55** (7), 41-52; *Ref. Zhur.*, *Khim.*, 1955, Abstr. No. 29,111.—The amperometric titration of Cu and other ions in 0.1 *M* KNO_3 with 20 per cent. of ethanol with Na anthranilate is studied by means of a dropping-mercury electrode. No external source of current is necessary for Cu. The pH should be between 4.5 and 5.5. Copper can be determined in the presence of Mg, and Cu and Pb can both be determined in the same soln. by first titrating Pb with Na_2SO_4 soln. and then Cu with anthranilate. Best results are obtained with 15 to 20 mg of Cu and 20 to 30 mg of Pb.

G. S. SMITH

2416. Controlled potential electrolysis. IX. Electrolytic separation of copper from bismuth by use of EDTA. Hisao Hayakawa, Masayoshi Ishibashi and Taitiro Fujinaga (Fac. Sci., Kyoto Univ., Sakyo-ku, Kyoto). *Japan Analyst*, 1955, **4** (10), 610-616.—The electro-deposition of Cu and Bi was studied in an aq. soln. containing NH_4NO_3 (supporting electrolyte) and EDTA (disodium salt). When the pH value is > 3.0 , the separate deposition of these metals is satisfactory in the presence of an amount of EDTA > 1.3 times the equiv. of the sum of Bi and Cu. The sample soln. containing Bi and Cu is treated with EDTA (disodium salt) (twice the equiv. of the sum of Bi and Cu), NH_4NO_3 (1 g) and hydroxylamine hydrochloride (1.5 g), the pH being adjusted to 3.1. The volume is made up to 10 ml and the product is electrolysed at -0.41 V *vs.* the S.C.E. at 50° to 60°C . The deposition of

Cu (≈ 60 mg) is quant., without contamination by Bi, in the presence of < 20 times the weight of Bi. At a pH higher than 5, when the EDTA complex of Cu is stabilised, the electrolysis proceeds too slowly.

K. SAITO

2417. Polarographic determination of traces of bismuth, iron, lead, antimony, nickel, cobalt and manganese in refined copper. A. J. Eve and E. T. Verdier (Rhodes Univ., Grahamstown, South Africa). *Anal. Chem.*, 1956, **28** (4), 537-538.—In the procedure described, Fe and Bi are pptd. from an ammoniacal soln. and, after dissolution of the ignited oxides, the Fe is determined polarographically in 0.3 *M* sodium tartrate as supporting electrolyte. A well-defined wave for Fe is obtained at -0.3 to -0.4 V *vs.* the S.C.E. The Bi is then determined in the same soln., after addition of F' and removal of O, the wave for Bi occurring at -0.5 V *vs.* the S.C.E. A second sample is used for the determination of Pb, Sb, Ni, Co and Mn, which are first separated from Cu by electro-deposition between platinum electrodes at a cathode potential of -0.51 V *vs.* an electrode of saturated Hg_2SO_4 in *N* H_2SO_4 and are then determined successively at 25°C in 0.1 *M* NaF as supporting electrolyte, the polarograms being taken ≈ 45 min. after preparing the soln. The waves for each metal are well defined and do not overlap at the concn. present in the samples. A complete analysis takes ≈ 14 hr. and the accuracy is within ≈ 4 to 5 per cent. for max. concn. of 0.02 per cent. of each metal. The method requires a sample of 30 g for refined Cu or 10 g for blister Cu.

W. J. BAKER

2418. Separation of small amounts of copper from nickel and cobalt by extraction of copper salicylaldehyde. I. P. Alimarin and V. V. Koreneva (M. V. Lomonosov Moscow Inst. Fine Chem. Technol.). *Zavod. Lab.*, 1956, **22** (4), 402-405.—The solubility of copper salicylaldehyde in a number of org. solvents has been determined. In CHCl_3 the solubility is 9.44×10^{-4} *M*. At pH 7 both Cu and Ni are extracted by CHCl_3 , but with increase of pH the amount of Ni extracted diminishes, whilst that of Cu remains constant. In ammoniacal soln. Cu can be separated from Ni. The soln. containing Cu and Ni is mixed with 1 ml of a 2 per cent. soln. of salicylaldehyde in ethanol, 8 ml of 25 per cent. aq. NH_3 and 10 ml of CHCl_3 ; the water phase is diluted to 15 ml and the mixture is shaken for 1 min. The Cu is removed from the CHCl_3 by shaking with 5 ml of 4 *N* HCl . The method is suitable for determining 1 pt. of Cu in 2000 pt. of Ni and is applied to the analysis of metallic Ni and Ni salts. To determine Cu and Ni in cobalt-containing ores, alloys and salts, 10 to 15 ml of a soln. of the sample containing > 0.25 to 0.30 mg of Cu and Ni and > 100 mg of Co are mixed with 2 ml of 4 *N* NH_4Cl , 5 ml of 20 per cent. aq. NH_3 and 1.5 ml of hydrogen peroxide (to oxidise the Co so that it is not extracted with CHCl_3) and boiled for 3 to 5 min. to remove excess of the oxidant and most of the NH_3 . The cooled soln. is transferred to a separating funnel, 1 to 1.5 ml of salicylaldehyde soln. and 10 ml of CHCl_3 are added, and the contents are shaken for 0.5 to 1 min. The Cu and Ni are in soln. in CHCl_3 ; they are extracted with 3 to 5 ml of dil. HCl (1+10), the acid soln. is treated with 0.5 ml of 2 per cent. salicylaldehyde soln. and 10 ml of 20 per cent. aq. NH_3 , and the Cu is extracted with 10 ml of CHCl_3 . Nickel remains in the aq. layer.

G. S. SMITH

2419. Flame-spectrochemical analysis. III.

Determination of magnesium in aluminium alloys. Shigerō Ikeda (Inst. of Steel, Tohoku Univ., Katabira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (10), 1122-1125.—The relationship between the intensity of the flame spectrum of Mg at 371 m μ (H, 4 lb per sq. in.) (O, 25 lb) and the concn. of Cu, Al, Mn, Fe and free acid was examined. These metal ions decrease the intensity of the Mg line to various extents. When the concn. of Al is >0.01 g per ml in HCl (<2 N), however, the intensity remains constant irrespective of the concn. of other ingredients, including other mineral acids. The working curve is linear for <0.25 mg of Mg per ml. The sample (1 g) is dissolved in HCl (1 + 1) (15 ml), oxidised with a small amount of HNO₃ and made up to 100 ml, then submitted to flame photometry. The average deviation is <10 per cent. for 0.4 to 2 per cent. of Mg, when the background is calibrated by the use of a 1 per cent. Al soln. in N HCl. K. SAITO

2420. Determination of magnesium in the presence of nickel, cobalt, zinc, copper and manganese. Sh. T. Talipov and A. T. Tashkhodzhaev. *Trudy Sredneaziat. Gosudarst. Univ. (Tashkent), Khim. Nauk.*, 1954, **55** (7), 145-149; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,137.—A standard soln. containing Mg as nitrate and a known amount of NiSO₄ was treated with a small amount of cryst. NH₄Cl, then conc. aq. NH₃ followed by excess of NaF, and centrifuged. The ppt. was separated, washed with ethanol, dried and weighed. The theoretical weight was obtained when the amount of aq. NH₃ added was just sufficient to form the complex $[\text{Ni}(\text{NH}_3)_6]^{2+}$. Magnesium can be determined in this way in the presence of 0.0125 to 0.0190 g of Ni, 0.0080 to 0.0175 g of Co, 0.0100 to 0.0350 g of Zn, and 0.0080 to 0.0250 g of Cu. Magnesium can be determined in the presence of Mn if 1.2 ml of conc. H₂SO₄ are added for each 70 ml of soln. The mean error is 0.18 per cent. The method is applicable to the analysis of alloys containing Mg. G. S. SMITH

2421. Volumetric titration of calcium fluoride.

Sh. T. Talipov, Z. T. Maksim'ycheva and B. K. Vandysheva. *Trudy Sredneaziat. Gosudarst. Univ. (Tashkent), Khim. Nauk.*, 1954, **55** (7), 151-154; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,136.—The finely ground sample (0.15 g) of fluor spar is heated with 10 ml of 10 per cent. acetic acid soln., and the insol. matter is dissolved by heating in either 30 ml of 5 per cent. FeCl₃ soln. acidified with 3.5 ml of 2 N HCl or 30 ml of 5 per cent. Cr(NO₃)₃ soln. acidified with 10 ml of 2 N HCl. The soln., diluted to a vol. of 100 to 120 ml, is treated with 3 g of tartaric acid and 2 to 2.5 g of oxalic acid, then boiled and neutralised with aq. NH₃ to restore the pale-yellow colour of the soln. The ppt. of Ca oxalate is washed, dissolved in H₂SO₄ and titrated with KMnO₄ soln. The error with the FeCl₃ process is ± 0.34 per cent., and that with the Cr(NO₃)₃ process is ± 0.31 per cent. The results agree satisfactorily with those obtained by Stark's classical method. G. S. SMITH

2422. Flame-spectrochemical analysis. IV.

Determination of calcium and magnesium oxides in basic slag. Shigerō Ikeda (Inst. of Iron, Steel and other Metals, Tohoku Univ., Katabira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (11), 1258-1261.—The intensity of the flame spectrum of Ca (554 m μ CaO band) is decreased with

increase in concn. of Al. It remains constant when the concn. of Al is >50 μ g per ml in a mineral acid soln. >0.05 N and is proportional to the concn. of Ca (0 to 100 μ g per ml). The intensity of the Mg line at 371 m μ is affected neither by Ca (1.2 to 1.5 mg per ml) nor by Al (0.3 to 1 mg) in HCl (<2 N), but that of the background is largely dependent on the concn. of Ca. No interference results from the presence of P, Fe and Mn under the given conditions. The sample (0.5 g) is dissolved in 6 N HCl (30 ml) and made up to 100 ml. A 25-ml portion is diluted to 500 ml after the addition of Al (25 mg) and submitted to flame photometry to determine the Ca. The Mg is measured by the use of the initial soln., the background being calibrated by the result for Ca. K. SAITO

2423. Compleximetric determination of calcium, magnesium, strontium and barium in pharmaceutical preparations. J. S. Faber (Pharm. Lab., Groningen Univ., Netherlands). *Pharm. Weekbl.*, 1956, **91** (5), 145-156.—A general account of compleximetric titrations is presented, with particular reference to the determinations of alkaline earths, alone or in mixtures. H. A. FISHER

2424. Indirect volumetric determination of barium and boron. O. Borchert (VEB Hartol-Werk, Magdeburg, Germany). *Chem. Tech., Berlin*, 1955, **7** (9), 554-555.—The quant. determination of Ba in the presence of Fe, Ca or Sr is achieved in ammoniacal or neutral soln. by pptn. with excess of 0.1 N K₂Cr₂O₇ and titration of unchanged reagent in the filtrate with 0.1 N Na₂S₂O₃ after adding KI soln. The gravimetric pptn. of boron as barium borotartarate, Ba₃B₂C₁₂H₂O₂₄ (*cf.* Gautier and Pignard, *Brit. Abstr. C*, 1951, 363) has been developed into an indirect volumetric determination of boron in (a) salts containing Ba, whereby the Ba is determined as above, before and after pptn. of the salt with an ammoniacal reagent containing 14 g of tartaric acid and 240 g of NH₄Cl per litre, and (b) salts free of Ba by using a precipitant containing 13 g of BaCl₂·2H₂O, 14 g of tartaric acid and 240 g of NH₄Cl per litre. Blanks are carried out on the reagents. S.C.I. ABSTR.

2425. Detection of zinc by means of tetramethyldiaminodiphenylantipyrinylmethanol. V. P. Zhivopistsev. *Uch. Zap. Molotov. Univ.*, 1954, **8** (3), 43-46; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,142.—The red soln. of tetramethyldiaminodiphenylantipyrinylmethanol (I) (0.06 g in 50 ml of 2 N HCl) and NH₄SCN (50 ml of 20 per cent. soln.) gives with Zn and certain other cations difficultly soluble blue complexes, e.g., (C₂₂H₃₁ON₄)₂Zn(SCN)₄. The minimum amount of Zn detectable is 2 to 3 μ g per ml, and the limiting dilution is 1 in 50,000. Alkali and alkaline-earth metals, Al, Mn, Fe^{II}, Cr and Ni do not interfere. Copper, Cd, Hg, Sb and Co also give a ppt. and interfere with the detection of Zn. I is synthesised by condensation of phenazone with Michler's ketone in the presence of phosphoryl chloride. G. S. SMITH

2426. Amperometric titration of zinc with anthranilic acid. A. K. Zhdanov and A. M. Yakubov. *Trudy Sredneaziat. Gosudarst. Univ. (Tashkent), Khim. Nauk.*, 1954, **55** (7), 53-64; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,112.—Zinc (15 to 50 mg in 50 ml) in soln. of KNO₃, Na₂SO₄ or Na acetate, containing 15 per cent. of ethanol, is titrated at pH 4 to 6 and at -1.4 V, with the use of a dropping-mercury electrode, with 0.17 M Na

anthranilate. Magnesium (24 to 486 mg) and Al (> 0.1 mole per litre) do not interfere in 0.05 M Na acetate. G. S. SMITH

2427. Determination of zinc in aluminium alloys by ion-exchange separation. Kazunobu Kodama and Teruyuki Kanie (Municipal Ind. Res. Inst., Rokuban-cho, Atsuta-ku, Nagoya). *Japan Analyst*, 1955, **4** (10), 627-629.—Zinc in aluminium alloys is adsorbed on the anion-exchange resin Amberlite IRA-410 (Cl) from 1 to 3 N HCl and eluted free from other constituents of the alloy with dil. HNO₃. The eluate is neutralised and titrated with EDTA (disodium salt). The use of a small amount of non-ionic surfactant is advantageous to decrease the necessary amount of the eluting agent. In the presence of Pb or Si, the HCl soln. of the sample is treated with H₂SO₄ and filtered. The filtrate is diluted, passed through a column of a cation-exchange resin and eluted with dil. HCl to convert the sulphates into chlorides. *Procedure*—The sample (0.5 g) is dissolved in HCl (1 + 1), evaporated, diluted to 200 ml with conc. HCl (35 ml) and water, treated with 3 per cent. H₂O₂ (2 to 3 ml) (to oxidise Cu⁺ to Cu²⁺) and passed through a column (15 ml) of Amberlite IRA-410, that has been treated with 2 N HCl (5 ml per min.). The column is washed with 0.1 N HNO₃ (200 ml) containing a non-ionic surfactant (18 per cent., 1 to 2 ml). The eluate is neutralised with aq. NH₃ (sp. gr. 0.88, 570 ml per litre of 1.3 M NH₄Cl) and titrated with EDTA (disodium salt) (0.015 N), with Eriochrome black T as indicator. In the presence of a large amount of Pb or Si, the HCl soln. is evaporated to dryness with H₂SO₄ (5 ml), diluted, filtered and made up to 500 ml. A 100-ml portion is diluted to 200 ml and passed through Amberlite IR-120 (NH₄); the resin is washed with water and eluted with 2 N HCl (200 ml). K. SAITO

2428. Separation of zinc from iron by means of alkali and electrolysis with a mercury electrode. E. F. Speranskaya, P. P. Ts'yb and M. T. Kozlovskii. *Uch. Zap. Kazakh. Univ.*, 1954, **16**, 72-78; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,144.—The use of NaOH both in hot and cold soln. for separating Zn (0.002 to 1 g) and Fe (0.0001 to 1.5 g) gives unsatisfactory results. Anodic oxidation of an amalgam of Zn and Fe in NaOH soln. is recommended. With c.d. of 0.001 to 0.01 amp. per sq. cm in N, 2 N and 3 N NaOH at 50° to 80° C, Zn is almost completely transferred into soln. The decomposition potential of zinc-iron amalgam at a c.d. of 0.001 amp. per sq. cm and 50° C is 1.3 V. The amalgam in N NaOH is polarised anodically with a c.d. of 0.001 amp. per sq. cm at 50° to 80° C, and electrolysis is stopped when the potential for oxidation of Fe is attained. The loss of Zn from an amalgam containing 0.0096 to 0.0250 g of Zn and 0.2500 to 1.00 g of Fe is 0.0004 to 0.0014 g. The efficiency of the separation is reduced by rise in temp. (at 80° C the loss of Zn is 0.0029 g) and by increase in the concn. of Fe (with 2 g of Fe and 0.025 g of Zn the loss is 2 to 3 mg). The method is applicable to the analysis of copper-zinc ores.

G. S. SMITH

2429. Precipitability of cadmium oxalate in the presence of its own and extraneous ions. M. P. Babkin, L. N. Nozhenko and E. I. Shevchenko. *Ukrain. Khim. Zhur.*, 1955, **21** (1), 93-96; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,086.—Cadmium oxalate is a ppt. that in the presence of its own kind of ion (cation and anion) shows at first a

reduced solubility and then increased solubility owing to a complex-forming reaction. In spite of the different forms of the crystals obtained from equivalent amounts of Cd²⁺ and C₂O₄²⁻ and from amounts in which one is present in excess, the chemical composition of the crystals is the same, CdC₂O₄·3H₂O. The presence in soln. of K⁺ and Cl⁻ greatly reduces the precipitability from soln. containing equivalent amounts of Cd²⁺ and C₂O₄²⁻. G. S. SMITH

2430. Separation of cadmium and iron by electrolysis with a mercury electrode. P. P. Ts'yb. *Uch. Zap. Kazakh. Univ.*, 1954, **16**, 79-85; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,145.—Electrolysis with a mercury electrode at -0.76 to -0.78 V at 20°, 50° and 80° C was carried out with electrolytes containing 0.0182 to 0.455 g per litre of Cd, and 0.0172 to 3.4509 g per litre of Fe in N H₂SO₄. With a soln. containing 18.2 mg of Cd and 0.0171 to 0.1725 g of Fe, Cd was completely deposited on the cathode without admixture of Fe. With increase in the content of Fe to 1.7252 and 3.4509 g the loss of Cd was 0.9 and 2.1 mg, and 4.9 and 36.5 mg, respectively, of Fe were deposited with the Cd. Anodic decomposition in N H₂SO₄ with and without an applied e.m.f. of an amalgam obtained by the cathode process was studied. With 16 mg of Cd and 17.2 mg of Fe in the amalgam both metals were completely separated. With increase of Fe to 0.6902 g some of the Fe appeared in the electrolyte. By a combination of the cathodic and anodic processes and repeating the electrolysis, 16 mg of Cd were completely separated from 3.3510 g of Fe. G. S. SMITH

2431. Determination of trace amounts of boron with two new colorimetric reagents. R. L. Grob and J. H. Yoe (Univ. of Virginia, Charlottesville, Va., U.S.A.). *Anal. Chim. Acta*, 1956, **14** (3), 253-262.—Two new colorimetric methods for the micro-determination of boron are based on the formation of a stable complex of boron with (i) 5-benzamido-6'-chloro-1:1'-dianthrimide (I), and (ii) 5-p-toluidino-1:1'-dianthrimide (II), both in 96 per cent. H₂SO₄ as solvent. The soln. should be heated at 130° C for 1.5 hr. to develop the max. intensity of colour. Beer's law is valid over the range of 1 to 5 µg of boron (per 10 ml of soln.) at 635 mµ for the complex with I, and from 1 to 4 µg at 720 mµ for the complex with II; the extinctions in both instances occur between 0.2 and 0.7 unit (1-cm cell). The corresponding sensitivities are 1 in 3 × 10⁸ and 1 in 2 × 10⁸, respectively. Provided that common metal ions and oxidising anions are removed initially, the methods are claimed to be accurate to within ≈ 0.001 µg of boron. The procedure can be applied to the determination of boron in fruit-tree leaves and lucerne (0.1 g) after decomposition with a mixture of H₂SO₄ (96 per cent.) and H₂O₂ (30 per cent.), followed by addition of methanol and distillation at 90° C. The distillate (ester and excess of methanol) is evaporated to dryness (i.r. lamp) with 5 ml of N aq. NH₃, the residue is cooled, the reagent soln. (I or II) is added and the extinction of the mixture is measured. The accuracy is within ≈ 1 p.p.m. of the boron recovered (≈ 99 per cent.). W. J. BAKER

2432. Analysis of boron tribromide and its addition compounds. W. J. Schuele, J. F. Hazel and W. M. McNabb (Univ. of Pennsylvania, Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (4),

505-507.—Samples of BBr_3 and its addition products with 5-nitroquinoline, quinoline and 4-picoline, respectively, were hydrolysed and the organic base was then removed with a cation-exchange resin (Amberlite IR-100) to yield an eluate containing only HBr and H_3BO_3 . These two acids were then titrated with standard aq. NaOH by four different methods, *viz.*, potentiometric, conductimetric, visual and spectrophotometric, with different acid-base indicators. The results show that the potentiometric and spectrophotometric methods are most satisfactory and are equally accurate, but that the latter method is quicker, mainly because no curve is needed to obtain the end-point, which occurs at 50 per cent. transmittance.

W. J. BAKER

2433. Use of oxine in the analysis of commercial aluminium sulphate. A statistical approach. A. Mendelowitz (African Explosives and Chem. Ind., Ltd., P.O. Northrand, Transvaal, S. Africa). *Anal. Chim. Acta*, 1956, **14** (3), 235-242.—The analysis of commercial $\text{Al}_2(\text{SO}_4)_3$ by pptn. of Al and Fe with oxine was studied statistically to determine the degree of control required for accurate results. Provided that correct conditions of pptn. are rigidly adhered to, the oxine method is much more accurate and precise than other methods. Recommended procedure—Transfer by pipette an aliquot (≈ 30 mg of Al) of the sample soln. to a beaker containing a weighed magnetic-stirrer bar, and oxidise any Fe by boiling with 10 per cent. HNO_3 (5 ml). Cool to $\approx 40^\circ\text{C}$, add excess (15.5 ml) of 2 per cent. oxine in N acetic acid and heat to 63°C . Switch on the magnetic stirrer. When the temp. has fallen to 60°C add 2 N ammonium acetate soln. at the rate of 2 ml per min. until pptn. starts and then a further 50 ml at the same rate. After ≈ 1 hr. filter the soln. through a No. 4 sintered-glass crucible, allowing the stirrer to enter the crucible with the ppt.; use exactly 250 ml of 1 per cent. ammonium acetate soln. for transferring the ppt. and washing it in the crucible. Do not let the ppt. suck dry until filtration is complete. Dry the ppt. at 140°C , cool for 30 min. (desiccator), place in the balance case for 10 min. and then weigh; repeat this procedure until the wt. is constant.

W. J. BAKER

2434. Thermogravimetric pyrolysis of 8-quinolinol and 5:7-dihalo-8-quinolinol chelates of scandium, thorium and uranium (VI). W. W. Wendlandt (Texas Technol. Coll., Lubbock, Tex., U.S.A.). *Anal. Chem.*, 1956, **28** (4), 499-501.—Thermogravimetric data for the 8-hydroxyquinoline (I), 5:7-dichloro-8-hydroxyquinoline (II) and 5:7-dibromo-8-hydroxyquinoline (III) chelates of Sc , Th and U^{VI} , respectively, indicate that only the complexes of Th and U^{VI} with I lose the extra mol. of solvation when heated. The const.-wt. levels for the two normal chelates of Th and U^{VI} with I are 250° to 310°C and 230° to 380°C , respectively, the corresponding oxides being formed completely at 600° and 450°C . The max. temp. for drying the complex of Sc with I is 125°C . The sublimation curves for the three chelating agents are shown. An excess of I can be removed from the ppt. by heating above 85°C . Sublimation of II occurs, without decomposition, between 142° and 250°C , whereas III sublimes and decomposes between 175° and 290°C .

W. J. BAKER

2435. The chemical analysis of the rare-earth elements. XI. Polarographic studies of praseodymium. Seizo Misumi and Akio Iwase (Fac. Lib.

Arts and Sci., Yamagata Univ., Koshirakawa-cho, Yamagata). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (11), 1231-1235.—The polarographic reduction wave of Pr was studied in a regulating soln. containing gelatin and LiCl or tetramethylammonium iodide (I). The reversible wave of Pr is clearly separated from that of H_3O^+ at $\text{pH} < 3.8$ in 0.1 M I. The half-wave potential remains constant (-1.85 V vs. the S.C.E.) for $< 10^{-3}$ M soln. of Pr and the wave height is proportional to its concn. The wave was analysed and it was found that the reduction corresponds to that from trivalent to elementary Pr .

K. SAITO

2436. High-frequency titrations involving chelation with ethylenediaminetetra-acetic acid. V. Complexation with rare earths. R. Hara and P. W. West (Louisiana State Univ., Baton Rouge, La., U.S.A.). *Anal. Chim. Acta*, 1956, **14** (3), 280-286.—High-frequency titrations over the range of pH 2.8 to 10 indicate that EDTA (disodium salt) reacts with rare-earth metals (La , Ce , Nd , Gd , Pr , etc.) in a 1:1 ratio forming stable complexes. In this respect, the rare-earth metals differ from Th , and they can be determined quant. (in milligram concn.) by direct high-frequency titration with 0.003 to 0.007 M EDTA (disodium salt) in acetate buffer at pH 5.3. Excellent end-points are obtained in the absence of oxalates or of excesses of other electrolytes. The error is ± 0.5 per cent.

W. J. BAKER

2437. Contribution to the study of the separation of rare-earth fission products using ethylenediaminetetra-acetic acid. G. Duyckaerts and J. Fuger (Univ. of Liège, Belgium). *Anal. Chim. Acta*, 1956, **14** (3), 243-246.—A rapid quant. separation of a mixture of milligram amounts of Y , Eu , Pm and Ce can be made by elution with EDTA (0.025 M) from a Dowex-50 resin column ($33\text{ cm} \times 1\text{ sq. cm}$, 36 to $74\text{ }\mu$) at 80°C . By elution at pH 3.05, Y , Eu and Pm are separated effectively in the first 80 ml of eluate; by raising the pH to 3.65 the Ce can then be eluted from the column in a min. vol. of eluate. The elution curves at various pH values are shown.

W. J. BAKER

2438. Rapid volumetric method for the determination of elementary carbon by decomposition with iodic acid. II. Some information on the application of the method for a simultaneous determination of graphite and amorphous carbon. Tomoo Takagi (Faculty of Sci., Kanazawa Univ., Kanazawa). *Japan Analyst.*, 1955, **4** (10), 624-627.—The rapid decomposition of elementary carbon (Kiba *et al.*, *Anal. Abstr.*, 1955, **2**, 2371) with KIO_3 in conc. H_3PO_4 was modified to enable a differential decomposition of graphite (I) and amorphous carbon (II) to be effected. The apparatus was slightly modified to prevent excessive loss of water during the decomposition, which results in a too viscous liquid and heterogeneous distribution of the temp. The ease with which the decomposition of I takes place increases by the use of a more conc. H_3PO_4 , whereas that of II is practically independent of the concn. When the decomposition of a mixed sample of I and II is carried out with orthophosphoric acid (sp. gr. 1.75), only II is decomposed at 245°C . The error is up to ± 3 per cent.

K. SAITO

2439. Spectrographic determination of silica. J. W. Anthony, R. J. Chandler, W. B. Huckabay and C. T. Kenner (Southern Methodist Univ.,

Dallas, Tex., U.S.A.). *Anal. Chem.*, 1956, **28** (4), 470-473.—A rapid quant. spectrographic procedure for the determination of > 70 per cent. of SiO_2 in shales, cherts and other rocks is described. By using pure Ge as internal standard, a very stable arc is produced in which the dry sample (1 to 2 mg) is completely and uniformly volatilised. Interference between the various other elements is eliminated by diluting the sample and Ge with powdered C in the ratio of 1 to 8. The developed spectrograms are measured microphotometrically to determine the absorbance ratio of the line pair Si 2881 Å - Ge 2556 Å. Two calibration curves are used, viz. from 0 to 20 per cent. of SiO_2 and from 20 to 70 per cent. of SiO_2 . The average difference from the gravimetric method is 1.0 to 1.2 per cent.

W. J. BAKER

2440. Use of oscillographic polarography in quantitative analysis. V. Determination of lead and cadmium in zinc and zinc salts. J. Doležal and P. Hofmann (Karlova Univ., Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (7), 1026-1029.—By means of the comparison-titration method of oscillographic polarography, Pb and Cd in Zn have been determined with a mean error of 2 to 7 per cent. The electrolyte consists of a mixture of 0.8 M ethylenediamine tartrate and 0.08 M $\text{K}_2\text{P}_2\text{O}_7$. The optimum concn. of Pb is 0.2 to 2.5 per cent., and of Cd 0.1 to 1.5 per cent.

G. GLASER

2441. Co-precipitation of lead with barium in the presence of excess of sulphuric acid. M. A. Popov (Central Lab. Western Siberia Geological Dept.). *Zavod. Lab.*, 1955, **21** (12), 1430-1431.—The difficulties of separating PbSO_4 and BaSO_4 are discussed. Decomposition by fusion with Na_2CO_3 or heating with Na_2CO_3 and ZnO, or spectrographic determination, is recommended.

G. S. SMITH

2442. Determination of hydrogen in titanium metal by hot extraction. R. K. Young and D. W. Cleaves (Titanium Metals Corp. of America, Henderson, Nev., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 372-374.—Hydrogen is determined by vacuum hot-extraction from samples of titanium metal at 900° to 950° C in a silica tube-furnace. The temp. and pressure of the H evolved are measured in a known vol. The sample (usually 3 g) is introduced into the furnace encased in a tin-foil capsule, for which a blank correction is applied. The determination is complete in 15 min. for powder, drillings, loose sponge and thin sheet samples, but thicker samples may require 30 to 40 min.

J. H. WATON

2443. Photometric determination of boron in titanium and its alloys. R. C. Calkins and V. A. Stenger (Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 399-402.—Boron in titanium and its alloys is determined photometrically as the carminic acid complex at 600 m μ after the removal of Ti as the peroxy complex on a cation-exchange resin. If any Ti comes through the column, a correction is made after determining the extinction of the Ti-carminic acid complex at 710 m μ . Good results are obtained for samples containing ≈ 0.1 per cent. of B, when the error is $\approx \pm 0.002$ per cent., but larger errors are obtained for contents of B of 0.005 per cent. Most common elements likely to occur in titanium alloys do not interfere. Interference from < 0.3 per cent. of V is negligible, but V must be removed if present in an amount ten times that of B.

J. H. WATON

2444. Colorimetric determination of zirconium with alizarin [red]. S. O. Gübeli and A. Jacob (Eidg. Tech. Hochsch., Zürich, Switzerland). *Helv. Chim. Acta*, 1956, **38** (4), 1026-1032.—Zirconium, which is known to polymerise in aq. soln., is present on the average as a triatomic ion from pH 3 to pH 1, but the complex breaks down at higher acidities. Heating for 10 min. will also cause the breakdown of the complex. The optimum range for the colorimetric estimation of Zr and Hf is pH 0.9 to 1.7, and for Th \approx pH 3. The extinction values also depend on the age of the soln., since they rise with increasing age. Interference is shown by F' and SO_4^{2-} (although small concn. are effective in breaking down the complex zirconium ion), but not by ClO_4^- , Cl^- and NO_3^- at concn. of 0.5 N at pH 1. Dissociation constants are given for the alizarin lakes of Zr, Hf and Th.

J. H. WATON

2445. Analytical aspects of some azo dyes from chromotropic acid. I. SNADNS dyes in the detection and volumetric determination of thorium. S. K. Datta (Gov. Coll., Darjeeling, India). *Z. anal. Chem.*, 1956, **149** (4), 270-277.—SNADNS (I) [1:8-dihydroxy-2-(4-sulphonaphth-1-ylazo)-naphthalene-3:6-disulphonic acid] (preparation described) and several closely related dyes form coloured complexes with Th and Zr and may be used for spot-tests (sensitivity about 2 to 4 μg). I and its 7-nitroso deriv. give coloured complexes with Ce^{IV} and with Ni and Co in aq. NH_3 . The dyes may be used as internal indicators in the determination of Th by oxalic acid at pH 2.2 to 3 and by EDTA, and of F' with $\text{Th}(\text{NO}_3)_4$.

II. Titrimetric determination of thorium with Versene using SNADNS dyes. S. K. Datta. *Ibid.*, 1956, **149** (5), 328-333.—SNADNS, or preferably (because of clearer colour changes) its 7-nitroso deriv. or di-SNADNS [1:8-dihydroxy-2:7-di-(4-sulphonaphth-1-ylazo)naphthalene-3:6-disulphonic acid], is a suitable indicator for the titration of Th^{IV} with EDTA at pH 2 to 3. The best results are obtained by adding an excess of EDTA (disodium salt) and back-titrating with a standard soln. of Th^{IV} . The accuracy on 20 to 75 mg of Th is within ± 0.5 to 0.2 mg. Alkaline earths, Fe, Zr, Cu and Au interfere and Th is separated from them by pptn. with phthalanilic acid. Lead, Zn, Hg, Co, Ni, Ce, Mn, Ti and Cr do not interfere. The accuracy may be improved by spectrophotometric determination of the end-point.

J. P. STERN

2446. Coulometric titration of ammonia with hypobromite. G. M. Arcand and E. H. Swift (California Inst. Technol., Pasadena, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (4), 440-443.—From 14 to 239 μg of NH_3 can be coulometrically titrated with electrolytically generated Br in a soln. at pH 8.5. A combined reagent and end-point correction is applied. The indicator current in the alkaline soln. is used only to indicate when a slight excess of Br has been generated, this excess being determined by acidifying the soln. with 9 M HClO_4 and again generating Br until a predetermined current value ($\approx 25 \mu\text{A}$) is obtained. The corrected time equals the titration time minus the reagent and end-point correction time. Neither Cu^{++} nor Hg^{++} (in concn. approx. equiv. to those used in a micro-Kjeldahl digestion) interfere, but Se should be removed before the titration is made. The error is within 0.4 μg .

W. J. BAKER

2447. Determination of water content of white fuming nitric acid utilising Karl Fischer reagent. M. L. Moberg, W. P. Knight and H. M. Kindsvater (Aerojet-General Corp., Azusa, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 412-413.—The sample of acid is first neutralised with an excess of a pyridine-dimethylformamide soln. (2:1, by vol.) to prevent its reacting with the reagent. An excess of Karl Fischer reagent is added, the excess being back-titrated to the dead-stop end-point with standard methanol-water soln. The results are accurate to within ± 1 per cent. (relative), but this figure rises fivefold in the presence of small amounts of dissolved salts. Amounts of $\text{NO}_2 < 1.5$ per cent. do not interfere. J. H. WATON

2448. Rapid volumetric determination of nitric acid or nitrate by reduction with ferrous salt. Tetsuro Murakami (Kogakuin Univ., Tsunohazu, Shinjuku-ku, Tokyo). *Japan Analyst.*, 1955, **4** (10), 630-633.—A rapid determination (12 to 15 min.) of nitrate was studied by means of reduction with Fe^{2+} , followed by titration of the resulting ferric ions with SnCl_2 . The reduction is complete within 5 min. (< 0.1 g of NO_3^-) in boiling 8.5 N HCl soln. in a current of CO_2 . The Fe^{3+} are titrated at $> 80^\circ\text{C}$ with 0.1 N SnCl_2 , the end-point being indicated by the decoloration of the yellow Fe^{3+} . The SnCl_2 soln. must be carefully stored. There is no interference from a large amount of alkali metals or SO_4^{2-} . This method can be used for the determination of HNO_3 in a mixture of conc. HNO_3 and H_2SO_4 , and for NH_4NO_3 in $(\text{NH}_4)_2\text{SO}_4$. K. SAITO

2449. Phenols as reagents for nitrites. S. Ya. Shnaiderman. *Ukrain. Khim. Zhur.*, 1955, **21** (1), 99-103; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,184.—Coloured soln. are obtained when M soln. of phenol, catechol, phloroglucinol, 1-naphthol, 2-naphthol, 2-hydroxynaphthoic acid and *p*-hydroxybenzoic acid are added to M NaNO_2 soln. The colour and its intensity depend on the acidity, concn. of NaNO_2 , the excess of the phenol and the duration of the interaction. Nitrate does not interfere. The min. amount of NaNO_2 detectable lies between 0.5 and 5 μg . To determine NO_2^- , the soln. (> 10 ml) containing 0.05 to 0.2 mg of NaNO_2 in a 25-ml calibrated flask is treated with 0.5 to 1.0 ml of 0.01 M 2-naphthol or other phenol and diluted to 25 ml with 5 N HCl. After 30 min. the extinction is measured by means of a photocolormeter, with a blue filter. G. S. SMITH

2450. Colorimetric determination of phosphorus in organic matter. M. Tanaka and S. Kanamori (Fac. Sci. Univ., Nagoya, Japan). *Anal. Chim. Acta*, 1956, **14** (3), 263-265.—In micro-determinations of P in organic matter and natural waters, the use of $\text{Fe}(\text{OH})_3$ as carrier to separate phosphate from other salts is proposed. *Procedure*—Heat the sample for 2 hr. with conc. H_2SO_4 (2 ml), FeCl_3 (≈ 5 mg of Fe^{III}) and HClO_4 (0.2 ml). Dilute the cooled contents with ≈ 70 ml of H_2O , heat to 75°C , neutralise with 4 N aq. NH_3 (bromocresol-purple indicator), cool and filter. Dissolve the ppt. in $\text{N H}_2\text{SO}_4$ (15 ml), add 2 per cent. ammonium molybdate soln. (1 ml) and 0.5 per cent. aq. hydrazine sulphate (1 ml) and make the soln. up to 25 ml with H_2O . Heat for ≈ 20 min. on a water bath, cool and then measure the extinction of the molybdenum-blue complex at 700 or 840 $\text{m}\mu$. The accuracy is good. W. J. BAKER

2451. Determination of phosphorus in ferro-phosphorus. I. M. Engal'chev and N. M. Bekker (Kharkov Works "Sickle and Hammer"). *Zavod. Lab.*, 1955, **21** (12), 1443-1444.—Ferrophosphorus (0.2 g) is dissolved in a mixture of 15 ml of H_2SO_4 and 5 ml of HNO_3 and, after treatment with KMnO_4 followed by NaNO_2 , the P is pptd. as ammonium molybdophosphate and determined alkalimetrically in the usual way. G. S. SMITH

2452. Analysis of phosphorus compounds. Rapid hydrolysis of condensed [poly]phosphates in volumetric analyses. E. J. Griffith (Monsanto Chem. Co., Dayton, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (4), 525-526.—The time required for the hydrolysis of polyphosphates (0.5-g sample) to orthophosphates during the analysis of samples by pH titration can be reduced from 8 hr. to 1 hr. by boiling the soln. (in conc. HCl) to dryness in the presence of KCl or NaCl (≈ 1 g) to prevent recondensation of the orthophosphate. The accuracy is within ± 0.5 per cent. W. J. BAKER

2453. Determination of triphosphate in commercial triphosphate and detergents built with triphosphate. H. J. Weiser, jun. (Proctor & Gamble Co., Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (4), 477-481.—Triphosphate ion ($\text{P}_3\text{O}_{10}^{4-}$) in commercial products can be determined, to within ± 0.8 per cent., by pptn. with an excess of 4 per cent. aq. tris(ethylenediamine)cobaltic chloride, i.e., $\text{Co}(\text{en})_3^{3+}$, at pH 3-6 and 40°C , and then measuring the excess of precipitant colorimetrically at 465 $\text{m}\mu$. Interference by co-pptn. of $\text{P}_2\text{O}_7^{4-}$ is provided for by a calibration curve and by rigid control of the pptn. High concn. of Na_2SO_4 in detergent samples are allowed for when making the calibration curves. Anionic detergent is almost completely removed by an initial extraction of the sample (≈ 3.5 g) in H_2O (25 ml) with 95 per cent. ethanol (400 ml); the insol. residue is dissolved in H_2O (100 to 150 ml) and any Na_2SiO_3 is partly removed by neutralisation with 0.5 N HCl (phenolphthalein indicator) followed by filtration of the diluted soln. The aliquot for the determination of $\text{P}_3\text{O}_{10}^{4-}$ should contain 0.20 ± 0.02 g of P_2O_5 ; for samples of commercial triphosphate, 10 ml of aq. Na_2SO_4 (≈ 1 per cent. w/v) are added. When 1 to 9 per cent. of phosphate glass (tetraphosphates, etc.) is present, or the $\text{P}_2\text{O}_{10}^{4-}$ content is < 50 per cent. of the total P_2O_5 , pptn. of $\text{P}_3\text{O}_{10}^{4-}$ is very incomplete, so that a known wt. of pure $\text{Na}_3\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ should be added and allowed for in calculating the result. One determination takes ≈ 2 hr., reproducibility being ≈ 0.5 per cent. Procedures for determining orthophosphate, trimetaphosphate and total P_2O_5 are also given. W. J. BAKER

2454. The paper-chromatographic separation and quantitative estimation of radioactive-labelled condensed phosphates. J. Meissner (Inst. exp. Biol. U. Med., Borstel, Germany). *Z. anorg. Chem.*, 1955, **281**, 293-302.—A method of separating condensed phosphates labelled with ^{32}P is described. The chromatographic technique used is that of Ebel and Volmar (*Brit. Abstr. C*, 1952, 377). The phosphates are detected by spraying with molybdate reagent (*cf.* Hanes and Isherwood, *Nature*, 1949, **164**, 1107) and by measuring the corresponding ^{32}P maxima. The arrangement for measuring the labelled condensed phosphates is described and their quantitative estimation is explained. By thermal condensation, very small amounts of

monophosphoric acid (< 1 mg of P) are observed to deviate from the normal course of condensation. As little as 10^{-6} g of P may be detected by this method.

C. A. SLATER

2455. A note on the determination of sodium phosphate. C. G. Butler and P. H. B. Ingle (Pharmacy Dept., Bradford Tech. Coll., England). *J. Pharm. Pharmacol.*, 1956, **8** (4), 264-265.—The end-point in the B.P. 1953 assay of sodium phosphate is unsatisfactory. The composition of the indicator should be changed from 1:1 to 4:1 bromocresol green-methyl red, and the end-point taken when the colour matches that of a buffer soln. (pH 4.5) containing the indicator.

A. R. ROGERS

2456. Coulometric titration of arsenic (III) solutions with cerium (IV). Spectrophotometric end-point detection. N. H. Furman and A. J. Fenton, jun. (Princeton Univ., Princeton, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (4), 515-517.—A spectrophotometric end-point procedure for the coulometric titration of 50 to 1000 μ g of As^{+++} with electrolytically generated Ce^{++++} in the presence of OsO_4 as catalyst is described. The end-point is detected by the max. extinction, at 320, 360 or 375 $m\mu$, of the excess of Ce^{++++} . The reagent blank is eliminated by generating Ce^{++++} to an arbitrary extinction, allowing the impurities to react, adding an excess of arsenous oxide, and then generating Ce^{++++} to an end-point determined by a curve of extinction vs. time. Successive samples can then be added and titrated coulometrically, the results being calculated by integrating the current-time values between any two successive end-points after the first. The max. error is ± 1.5 per cent.

W. J. BAKER

2457. Spectrophotometric determination of arsenic in refined gold with ammonium molybdate and hydrazine sulphate. J. O. Perzyna. *Bol. Soc. Chim. Peru*, 1955, **21**, 47-51.—The sample of Au (2 to 25 g) is dissolved in aqua regia (10 to 20 ml) and heated to remove oxides of N; the residue is dissolved in dil. HCl and made alkaline with KOH soln. (10 per cent.) (20 ml). Solid hydrazine sulphate is then added in small portions and the Au, which is thus reduced to the metallic state, is filtered off and washed with dil. aq. KOH soln. The filtrate, containing the As as potassium arsenite, is neutralised with conc. HCl and transferred to an arsine apparatus (at 70° to 80°C). Granulated Zn (2 g) is then added, followed by conc. HCl (5 ml), dropwise. The AsH_3 is collected in a solution containing $HgCl_2$, H_2SO_4 and $KMnO_4$. Ammonium molybdate-hydrazine sulphate reagent is then added, the mixture is warmed for 15 min. and the molybdenum blue is determined spectrophotometrically at 840 $m\mu$ or 625 $m\mu$.

L. A. O'NEILL

2458. Derivatives of thiourea as reagents for the determination of bismuth. M. P. Makukha. *Sb. Ref. Nauch. Rabot. Teor. Kaf. L'vov Med. Inst.*, 1954, (1), 94-95; *Ref. Zhur., Khim.*, 1955, (15), Abstr. No. 31,889.—The influence of various substituents and their positions on the intensity of the colour of bismuth complexes with derivatives of thiourea (acetylthiourea, methylthiourea, allylthiourea, diphenylthiourea, methylphenylthiourea, phenylthiourea, di-*p*-ethoxyphenylthiourea, and di-*o*-, *m*- and *p*-tolylthiourea) has been studied. All the derivatives studied, with the exception of acetylthiourea and 6-methylthiouracil, form intensely yellow complexes. The most sensitive reagent

for the detection of Bi is di-*o*-tolylthiourea, the bismuth complexes of which are about 10 times more intensely coloured than those of unsubstituted thiourea.

C. D. KOPKIN

2459. Use of catecholsulphonophthalein in colorimetric analysis. I. Photometric determination of bismuth. M. Svach (Inst. anal. Chem., Montan-hochsch., Ostrau, Czechoslovakia). *Z. anal. Chem.*, 1956, **149** (5), 325-328.—Catecholsulphonophthalein (catechol violet) (*cf.* Vodak and Leminger, *Chem. Listy*, 1954, **48**, 552) at pH 2 to 4 forms a blue complex with Bi and a red complex with Th; at pH 6.5 it gives a blue complex with Cu. The bismuth complex is suitable for photometry, the extinction at 610 $m\mu$ being determined after 20 min. The Beer-Lambert law holds for concn. of Bi of 400 μ g to 2400 μ g per cent. There is no interference from Pb, Cu, Cd, Ag, Co, Ni, Mn, Zn, Al, Ca, Mg, Be, Sr, Na, K and NH_4^+ , but Fe^{III} and Th should be absent. Large amounts of Cl^- and PO_4^{---} , and complexing anions, interfere.

J. P. STERN

2460. Bromimetric determination of vanadium (V) by hydrazine. G. S. Deshmukh and M. G. Bapat (Hindu Univ., Benares, India). *Anal. Chim. Acta*, 1956, **14** (3), 225-227.—From 0.02 to 0.12 of V^V can be quant. determined by reduction to V^{IV} with hydrazine in 4 to 5 N HCl, followed by back-titration of the excess of hydrazine with standard $KBrO_3$ soln., with the dead-stop end-point method. There is no oxidation of V^{IV} by $KBrO_3$, and the accuracy is high.

W. J. BAKER

2461. Photometric determination of vanadium in iron sand by diphenylaminesulphonate method. Shizo Hirano and Tsutomu Fukazawa (Inst. Techno-Anal. Chem., Fac. Eng., Nagoya Univ., Chigusa-ku, Nagoya). *Japan Analyst*, 1955, **4** (10), 616-621.—The colorimetric determination of a small amount of V (< 0.5 per cent.) in iron sand with Na diphenylaminesulphonate (I) was examined (Meaurio, *Ann. Chim. Anal.*, 1913, **23**, 47) and its use for rapid (< 25 min.) analysis studied. The colour (max. absorption, 560 $m\mu$) is stabilised by the presence of $Fe_2(SO_4)_3$ (50 to 500 mg per 100 ml) and phosphate. For the oxidation of V, the use of $KMnO_4$ is most suitable, its excess being decomposed with $NaNO_2$. *Procedure*—The sample (0.1 g) is decomposed with H_3PO_4 (15 ml), then H_2SO_4 (1 + 1) (40 ml) and sufficient Fe^{+++} are added to produce 100 ml containing 0.05 to 0.5 per cent. of Fe. The soln. is then treated with urea (20 per cent. soln., 5 ml) and 1 per cent. $KMnO_4$ until the purple colour persists for > 3 min. Sodium nitrite soln. (3 per cent.) is added until a clear soln. is obtained and the whole is made up to 100 ml together with I (0.05 per cent. aq. soln., 2.0 ml). The extinction is measured at 520 to 600 $m\mu$ within 10 min. The soln. in the cell is treated with a few drops of $FeSO_4$ and the extinction is again measured. The amount of V is calculated from the difference of the two measurements. The error is $\approx \pm 3 \mu$ g of V.

K. SAITO

2462. Photometric determination of vanadium and molybdenum in the presence of each other by means of catechol. V. Patrovský (Ústřední ústav geol., Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (6), 854-857.—A rapid and sensitive method for the determination of V and Mo in the presence of each other, based on the formation of coloured complexes with catechol, is described. With V^{IV} ,

catechol gives a blue complex with max. extinction at 600 $m\mu$, whilst with Mo an orange complex with max. at 430 $m\mu$ is formed. Iron, Ti and Mn interfere; Al in concn. > 20 mg per 50 ml must be masked with F^- . *Determination of V and Mo in ores*—Evaporate the finely powdered sample (0.5 to 1 g) in a platinum dish with H_2SO_4 (1 + 1) (0.5 ml) and 40 per cent. HF (2 to 3 ml) to white fumes. Ignite the residue at a temp. $> 500^\circ C$ to prevent loss of volatile MoO_3 , then fuse it with $NaKCO_3$ (2 to 4 g), borax (0.5 to 1 g) and KNO_3 (a small crystal), digest the melt with hot H_2O , add a few drops of 3 per cent. H_2O_2 , boil and filter. Wash the residue well, acidify the combined filtrates with HCl to methyl orange, destroy the indicator with a drop of bromine water, concentrate the soln., cool and dilute to 50 or 100 ml. Treat an aliquot (10 to 25 ml) with a saturated soln. of Na_2SO_3 (1 ml), and, after a few sec., with a 20 per cent. soln. of catechol in aq. ethanol (5 ml), followed by solid Na or ammonium acetate (1 to 2 g) and 10 per cent. NH_4F (0.5 to 1 ml). Dilute the soln. to 50 ml and measure the extinction at 600 and 430 $m\mu$ for V and Mo, respectively. *Determination of V and Mo in steel*—Decompose the sample by fusion with Na_2O_2 , boil with H_2O_2 to remove Mn, then proceed as above. Much Cr and W interferes.

G. GLASER

2463. Determination of niobium in alloys. E. G. Vavilova and G. F. Khaladzh. *Trudy Inst. Chern. Metall. Akad. Nauk Ukrain. SSR*, 1954, **8**, 89-96; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,163.—The alloy (0.2 to 1.0 g) is attacked with boiling conc. HCl (15 to 20 ml), the soln. is evaporated to 10 ml, and the insol. matter containing 70 to 86 per cent. of the Nb is filtered off and washed with hot dil. HCl (1 + 50). The residue is ignited, fused with $K_2S_2O_7$, dissolved in hot water and added to the filtrate. The soln. (100 ml) is boiled for 15 min. with additions of water to maintain the bulk, then set aside in a warm place for 1 to 2 hr. and filtered. The ppt. is washed with hot dil. HCl (1 + 50) until the washings give a negative reaction for Fe^{+++} with KSCN, and then ignited in Pt at 1000° to $1050^\circ C$. If the Nb_2O_5 is coloured it is fused again with $K_2S_2O_7$. With 0.35 g of Cr or 0.60 g of Ni in 100 ml of dil. HCl (1 + 10) containing 0.0132 g of Nb the amount of Cr or Ni pptd. with the Nb_2O_5 is 5.8 to 7.0 mg. With 0.335 g of Fe and 0.015 g of Nb in 100 ml the amount of Fe pptd. is 0.3 mg. Fusion of the ppt. with $K_2S_2O_7$ frees it from impurities. The method has been used for the analysis of 18 different alloys containing 0.20 to 7.70 per cent. of Nb. With the lower contents the relative error of the determination is 5 per cent.

G. S. SMITH

2464. Determination of sulphur in coal and coke by Sheffield high-temperature method. R. A. Mott and H. C. Wilkinson (British Coke Res. Ass., 74, Grosvenor St., London). *Fuel, Lond.*, 1956, **35** (1), 6-18.—The rapid combustion method (*Anal. Abstr.*, 1955, **2**, 2372) gave duplicates differing by > 0.03 per cent. of S on coal and coke samples, with an oxygen rate of 300 ml per min., a single disc absorber of sintered glass (No. 3 porosity) and heating at a rate so as to reach $1350^\circ C$ in 6 min. The simultaneous determination of S and Cl takes 20 min. Agreement with Eschka results is good. With a view to international standardisation, combustion at $> 1250^\circ C$ with an oxygen rate of 700 ml per min. and a covering layer of $FePO_4$ to ensure the decomposition of $CaSO_4$, as

in the German standard method, was found satisfactory. Kaolin is equally effective in decomposing $CaSO_4$ and is preferable to $FePO_4$.

A. R. PEARSON

2465. The compleximetric determination of hydrogen sulphide. M. J. Maurice (*Anal. Lab. Artificial Silk, Holland*). *Chem. Weekbl.*, 1956, **52** (8), 122.—The method recommended for the determination of H_2S is based on the absorption of the gas in cupric acetate soln., filtering off the CuS and titrating an aliquot portion of the filtrate with EDTA (disodium salt). The materials required are (a) EDTA (disodium salt) (0.02 N), (b) murexide (0.1 g ground in a mortar with 20 g of pure NaCl, (c) $(CH_3COO)_2Cu \cdot H_2O$ soln. (0.02 N) (1.9964 g and 120 ml of 2 N acetic acid made up to 1 litre), (d) aq. NH_3 (4 N), and (e) tartaric acid. The H_2S is driven through two wash-bottles, each containing 25 ml of soln. (c), by a fairly rapid stream of N for 15 min. The contents of the wash-bottles are then made up to 200 ml and filtered, the first 25 ml being rejected. To 100 ml of the remaining filtrate are added 20 to 30 mg of (e), 100 mg of mixture (b), and sufficient of soln. (d) to turn the soln. just green, plus a further three drops. The mixture is then titrated with soln. (a). The method gives reliable results for the determination of 0.5 to 10 mg of H_2S .

P. HAAS

2466. Effect of ageing solutions of barium chloride on particle size of barium sulphate. E. J. Bogan and H. V. Moyer (Ohio State Univ., Columbus, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (4), 473-476.—A large increase in particle size of $BaSO_4$ crystals occurs when aged (1 to 6 days) or filtered soln. of $BaCl_2$ (1 to 5 per cent. w/v) are used for pptn. The particle size depends inversely on the number of nuclei that are available as foci for crystallisation, these nuclei being very probably aggregates of incompletely dissolved $BaCl_2$ in the fresh unfiltered soln. Adsorption of air on the surface of fine crystals of $BaCl_2$ may cause these to persist during ageing of the soln. Filtration through a fine filter removes most of these nuclei.

W. J. BAKER

2467. Volumetric determination of sulphate by the use of sodium palmitate. Hisakazu Nakata and Yuzuru Kusaka (*Fac. Sci., Konan Univ., Higashinada-ku, Kobe*). *Japan Analyst*, 1955, **4** (10), 621-623.—Sulphate ions are pptd. with Ba^{++} and the excess of Ba^{++} is pptd. with Na palmitate (I). I is potentiometrically titrated with H_2SO_4 in a mixture of ethanol and benzene or carbon tetrachloride (1 + 1). Sulphate ions (1 to 10 mg) are pptd. with $BaCl_2$ (0.005 M, 20.0 ml) and the soln. is evaporated almost to dryness on a water bath. The product is treated with I (0.005 N in ethanol, 50 ml), then filtered and washed with warm ethanol. Both ethanolic soln. are combined, treated with an equal volume of benzene and potentiometrically titrated.

K. SAITO

2468. Technique of determining sulphate in sea water. O. V. Shishkina. *Trudy Inst. Okeanol. Akad. Nauk, SSSR*, 1954, **8**, 253-268; *Ref. Zhur., Khim.*, 1955, Abstr. No. 23,982.—To determine SO_4^{--} in alkali-metal salt solutions and in sea water the $BaCl_2$ solution should be added rapidly in a stream to hinder co-pptn. of alkali-metal sulphate, but in pure H_2SO_4 solutions the addition should be made slowly in drops to prevent pptn. of $BaCl_2$.

G. S. SMITH

2469. Volumetric estimation of selenite and tellurite with alkaline permanganate. I. M. Issa and R. M. Issa (Cairo Univ., Giza, Egypt). *Chemist Analyst*, 1956, **45** (1), 16-18.—Selenite and tellurite are estimated with alkaline permanganate without heating, telluric acid being added to prevent the pptn. of MnO_2 , which would produce catalytic effects. *Procedure*—To 25 ml of a KMnO_4 soln. of suitable concn. are added ≈ 0.1 g of telluric acid and enough 5 N NaOH to make the soln. 0.1 to 2.0 N in alkali. The selenite or tellurite soln. is introduced and is well mixed. The reaction mixture is poured into 40 ml of ice-cold ferrous ammonium sulphate soln. to which enough 6 N H_2SO_4 has been added to neutralise all the alkali and to leave the final soln. 2 N in acid. The excess of Fe^{++} is titrated with KMnO_4 in the presence of H_3PO_4 . An oxalic acid soln. may replace that of ferrous ammonium sulphate, when no cooling is necessary. In an alternative procedure, 5 ml of selenite or tellurite soln. are mixed with ≈ 0.1 g of telluric acid and made alkaline, as described above. After the addition of 10 ml of KMnO_4 soln., with stirring, the analysis is completed as before.

J. H. WATON

2470. Alkalimetric determination of telluric acid in the presence of polyhydric alcohols. J. O. Edwards and A. L. Laferriere (Metcalf Chem. Lab., Brown Univ., Providence, R.I., U.S.A.). *Chemist Analyst*, 1956, **45** (1), 12-16.—Propane-1:2-diol is the most suitable of the polyhydric alcohols studied for sharpening the end-point in the titration of telluric acid. It is selected because of its ready availability in a pure condition, and because it has a high rate of combination with the tellurate ion. The end-point is best found by plotting a pH curve, since the behaviour of indicators is dependent on the amount of the glycol used, and the colour change is poor. *Procedure*—For telluric acid soln. in the range 0.1 to 0.5 M, the use of 20 ml of propane-1:2-diol in a total of 100 ml of soln. is recommended when a pH meter is employed to detect the end-point, but only 10 ml if phenolphthalein is used. The reproducibility of the results is within ± 0.2 and ± 0.5 per cent., respectively.

J. H. WATON

2471. Separation by paper chromatography of the ions Cr^{++} , Cr^{+++} and CrO_4^{--} . C. Bigli (Chem. Inst., Univ. Ferrara, Italy). *Ann. Chim., Roma*, 1955, **45** (12), 1087-1090.—The separation of Cr^{++} , Cr^{+++} and CrO_4^{--} has been effected by a procedure similar to that used for ions of the different valency states of Fe, Hg and Cu (cf. *Ibid.*, 1955, **45**, 532). The efficiency of various solvents and mixtures has been compared, the best results being obtained with butanol-acetic acid-ethyl acetoacetate- H_2O (50:10:5:35), and an ascending technique.

L. A. O'NEILL

2472. Colorimetric estimation of molybdenum in stainless and chrome-molybdenum steel, using phenylhydrazine. L. Pennec, A. Mutte and M. Monnier (Lab. Centre d'Études Vallourec à Aulnoye, Nord, France). *Chim. Anal.*, 1956, **38** (3), 94-95.—Phenylhydrazine forms a stable red complex with Mo in acid soln. which can be used for estimating up to 5 per cent. of Mo in steel. The method is rapid and interference by elements normally present is negligible. *Procedure*—Dissolve a portion of the sample containing 0.5 to 1.0 mg of Mo in conc. HCl (10 ml), add H_2O_2 (2 ml) and evaporate almost to dryness. Re-dissolve in water, add ≈ 10 ml of

dil. HCl (1 per cent.), saturated with SO_2 to reduce Fe^{+++} , and boil to remove excess of SO_2 . Add acetic acid (50 per cent.) (50 ml) and filter off any pptd. Si. Boil the soln. with solid phenylhydrazine hydrochloride (1.5 g) for 5 min. Introduce 25 ml of conc. acetic acid, cool and dilute to 100 ml. Compare the extinction at 500 m μ in a 1-cm cell with that of a blank soln. made by omission of the phenylhydrazine and the boiling.

D. G. FORBES

2473. A comparative study of some methods for the quantitative determination of tungsten. A. F. Nemirovskaya, *Trudy Komissii Anal. Khim. Akad. Nauk SSSR*, 1954, **5** (8), 207-214; *Ref. Zhur., Khim.*, 1955, (15), Abstr. No. 31,893.—The methods studied are based on the pptn. of W by $\text{Hg}_2(\text{NO}_3)_2$ soln., by cinchonine, benzidine hydrochloride, gelatin, acid hydrolysis and the acidimetric procedure of Dymov. For the determination of small quantities of W (from 1 to 9 per cent.) in steel, sufficiently accurate results are obtained by the cinchonine and gelatin methods, and by the accelerated gravimetric methods of Dymov.

C. D. KOPKIN

2474. Analysis of samples containing uranium, niobium and zirconium. P. J. Elving and E. C. Olson (Univ. Michigan, Ann Arbor, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 338-342.—Electrometric methods are given for the analysis of U and Zr when present together with or without Nb. When Nb is not present, U is estimated polarographically between 0.0 and -0.5 V vs. the S.C.E., and Zr by an amperometric titration at -1.0 V vs. the S.C.E. with a standard cupferron soln., on separate aliquots of the soln. of the sample in 10 per cent. H_2SO_4 . When Nb is present, Zr is separated as its phosphate in the presence of H_2O_2 , and the suspension in 10 per cent. H_2SO_4 is titrated with cupferron. The U and Nb are determined polarographically in conc. HCl. The average errors for U, Nb and Zr are ± 1.0 , ± 1.0 and ± 0.5 per cent. (relative), respectively. The method has been applied successfully to the determination of Nb in an ore. The material is brought into soln. by fusion with K_2CO_3 , thereby eliminating Fe and Ti, which would interfere.

J. H. WATON

2475. Colorimetric determination of small amounts of fluoride with "Neo-thorin." I. Fundamental conditions for analysis. Koichi Emi and Tadashi Hayami (Fac. Sci., Okayama Univ., Okayama). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (11), 1291-1293.—A new reagent "Neo-thorin," o-(1:8-dihydroxy-3:6-disulpho-2-naphthylazo)-benzenearsonic acid (I) (max. absorption, 500 m μ in an aq. soln. of pH 2.3) was synthesised and the use of its thorium complex (max. absorption, 570 m μ at pH 2.3) for the determination of F (< 50 μg in 50 ml) was studied. The extinctions of both I and its complex with Th are sensitive towards change in pH, but remain constant between pH 2.1 and 2.4, the extinction of the complex decreasing in proportion to the amount of F^- . Common ions, including Cl^- , SO_4^{--} , PO_4^{--} , Al, Fe, Ca and Mg, interfere. Any F in the sample is distilled from an H_2SO_4 soln. in the presence of SiO_2 . The time taken for an estimation is < 1 hr.

K. SAITO

2476. Comparative studies on the micro-determination of fluorine. Wataru Funasaka, Makoto Kawane, Tsuguo Kojima and Kokichi Ishihara (Fac. Eng., Kyoto Univ., Sakyo-ku, Kyoto).

Japan Analyst, 1955, **4** (10), 607-610.—Colorimetric methods for the determination of a micro amount of F^- by means of the decoloration of ferric thiocyanate (I), ferric salicylate (II), Th-alizarin (III), Zr-alizarin and Al-haematoxilin were compared. The results are statistically analysed and the interference by other ions is discussed. The method with II is affected by CO_3^{2-} , and the methods with I and III are affected by SO_4^{2-} . For ≈ 10 p.p.m. of F^- , the ferric salicylate method is the best, and for < 5 p.p.m. of F^- the alizarin methods are the most satisfactory. K. SAITO

2477. Analytical aspects of some azo dyes from chromotropic acid. III. Use of SNADNS dyes in the volumetric determination of fluorine. S. K. Datta (Gov. Coll., Darjeeling, India). *Z. anal. Chem.*, 1956, **149** (5), 333-339.—SNADNS, or preferably its 7-nitroso deriv., and di-SNADNS (cf. *Anal. Abstr.*, 1956, **3**, 2445) are used as indicators in the volumetric determination of F^- at pH 2 to 2.4 with $Th(NO_3)_3$. Minerals containing F are pretreated (fusion with $ZnO-Na_2CO_3$ and distillation with $HClO_4-H_3PO_4$) to liberate F^- . Thorium nitrate is added to the F^- soln. containing the indicator, the end-point being shown by formation of the coloured Th-indicator lake. Iron, Cu, Sn, Zr and Au interfere. The method is applicable on the macro- and on the micro-scale. The accuracy on 20 to 50 mg of F^- is within ± 1 to 2 per cent., and on 20 to 75 μg of F^- within $\pm 3 \mu g$.

J. P. STERN

2478. Radiometric determination of inorganic fluoride. E. I. Onstott and W. P. Ellis (Univ. Calif., Los Alamos Sci. Lab., N.M., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 393-397.—A radiometric determination of F^- is investigated in which the sample is titrated with Sm^{3+} containing Eu^{3+} as carrier tracer. Various excess amounts of titrant are added, and the activity of the soln. is measured. The end-point is obtained by extrapolating back to zero activity. Difficulty is encountered in the pptn. of lanthanon fluoride, which tends to be colloidal. Soln. of ≈ 0.1 M NaF are estimated with errors < 1 per cent. When applied to soln. of Na_2SiF_6 , the method gives less satisfactory results. In a micro-titration of 0.01 M soln. of NaF, with a soln. of 0.024 M Na acetate in *M* acetic acid as a flocculator, good results are obtained. Interference is shown by Fe^{3+} , Ni^{2+} and Cr^{3+} .

J. H. WATON

2479. Oscillometric determination of fluoride. C. L. Grant and H. M. Haendler (Univ. of New Hampshire, Durham, N.H., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 415-418.—A rapid method adaptable to automatic recording is described for the determination of macro quantities of fluoride. A modification of the Willard and Winter steam-distillation procedure (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 7) is used. After accurate adjustment of the pH to 5.90 ± 0.02 , titration with thorium nitrate is carried out, a high-frequency oscillogram being used for end-point detection. The average accuracy for soln. containing 3 to 8 mg of fluoride per 100 ml was within 0.2 per cent.

K. A. PROCTOR

2480. Oxidations with alkaline permanganate using univalent thallium for the back-titration. II. Determination of iodate, iodide and ferrocyanide. I. M. Issa and A. A. Abdul Azim (Cairo Univ., Egypt). *Anal. Chim. Acta*, 1956, **14** (3),

217-224.—By using the procedure described previously (*Anal. Abstr.*, 1954, **1**, 1807) the determination of I^- , IO_3^- or $Fe(CN)_6^{4-}$ can be effected by oxidation with excess of $KMnO_4$ soln. (≈ 0.1 N) in the presence of *N* NaOH and Ba^{2+} ($\equiv Mn_2O_7$ concn.), followed by electrometric titration of the excess of $KMnO_4$ with univalent Tl (0.04 N). For samples of IO_3^- the addition of Ba^{2+} should not be made until just before the titration is begun. The results tend to be inaccurate if the variables are not closely controlled; the oxidation reactions are discussed. W. J. BAKER

2481. Flame-photometric determination of manganese in cement. J. J. Diamond (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 328-329.—No previous chemical separations are necessary with this method and the same sample soln. can be used for the determination of Na, K and Sr. The measurements are made at 403.3 $m\mu$, where Mn gives a very sharp peak. A correction for background emission is made by subtracting the emission at 401.0 $m\mu$. *Procedure*—The sample of cement (1 g) is suspended in water, dissolved in 5 ml of conc. HCl and digested. The soln. is filtered and made up to 100 ml, and the emission of the soln. is compared with that from standard soln. prepared from a cement of low manganese content to which known amounts of standard manganese soln. have been added. The results are in good agreement with those obtained colorimetrically. J. H. WATON

2482. Available oxygen in manganese dioxide. M. J. Katz, R. C. Clarke and W. F. Nye (Signal Corps Engng Lab., Fort Monmouth, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (4), 507-508.—Good agreement between the available oxygen contents of MnO_2 , as determined by the $FeSO_4$ and Na oxalate methods, can be obtained normally only on natural pyrolusites. On synthetic MnO_2 samples, the oxalate method gives results from 1 to 4 per cent. too high owing to varying degrees of air oxidation of the oxalate. It is recommended that the oxalate procedure should be conducted in an atm. of CO_2 or N.

W. J. BAKER

2483. Cerimetry. I. Cerimetric titration of very small amounts of bivalent iron in presence of some oxidisable ions. A. Petzold (Bergakademie, Freiberg, Saxony, Germany). *Z. anal. Chem.*, 1956, **149** (4), 258-263.—Small quantities (0.1 to 3 mg) of Fe^{II} in the presence of As^{III} and Sb^{III} are determined with $Ce(SO_4)_2$ with an accuracy within ± 0.02 mg. In H_2SO_4 or acetic acid soln. (up to 3 per cent.), ferroin is used as indicator, but in HCl soln. methyl red is preferred. Bivalent tin reacts with $Ce(SO_4)_2$ and generally interferes if present in more than half the amount of the Fe, but, in the presence of small amounts of Sn^{II} , Fe may be determined with satisfactory accuracy. The method is useful in toxicological analyses. J. P. STERN

2484. Compleximetric determination of iron in presence of Variamine blue as indicator. L. Erdely and G. Rády (Inst. Gen. Chem., Tech. Univ., Budapest, Hungary). *Z. anal. Chem.*, 1956, **149** (4), 250-257.—Variamine blue B (with NaCl as solid diluent) is a useful redox indicator for the compleximetric determination of Fe^{III} at pH 1.7 to 3 and at room temp. Results on 5 to 30 ml of 0.01 N $FeCl_3$ are accurate to within ± 1 per cent. and on 5 to 20 ml of 0.1 N $FeCl_3$ to within ± 0.4 per cent. Ammonium ions, Hg^{II} , Ca, Sr, Ba, Mg,

K and Na (all in mol. ratio to Fe of 1:10) and Zn and Mn^{II} (1:1) do not interfere, but Cu, Bi and Co (1:1) interfere. Acetate, Cl⁻, NO₃⁻ and SO₄²⁻ do not interfere, but F⁻ and PO₄³⁻ do. *Procedure*—Treat the sample of FeCl₃ with 10 per cent. aq. NH₃ until a slight permanent ppt. appears, and then adjust the pH to between 1.7 and 3 with 2 N formic acid (1 to 5 ml). Dilute the soln. to 100 ml, add the indicator, and titrate immediately with 0.05 M or 0.01 M EDTA (disodium salt), rapidly at first then dropwise to a yellow end-point.

J. P. STERN

2485. Coulometric titration of iron (III) with electrolytically generated iron (II) - ethylenediamine-tetra-acetate. R. W. Schmid and C. N. Reilley (Univ. of North Carolina, Chapel Hill, N.C., U.S.A.). *Anal. Chem.*, 1956, **28** (4), 520-522.—Coulometric titrations of Fe⁺⁺⁺ with electrolytically generated Fe⁺⁺-EDTA can be made manually or automatically at pH 2.5 in the presence of N and in the absence of sunlight, by using Fe⁺⁺⁺-EDTA soln. as supporting electrolyte. The error is ± 1.0 per cent. *Procedure*—Fill the cell (illustrated) with 25 to 30 ml of Fe⁺⁺⁺-EDTA soln. (0.05 M for titrations at currents ≥ 4 mA, 0.1 M for a current of 43 mA) and de-aerate for 10 min. with N. After the addition of a few ml of the soln. to be titrated make a pre-titration; then add the sample soln. (5 ml) and titrate. The distance between the two end-points represents the titre of the sample. With a current of 43 mA (high contents of Fe in the sample), the titration curves can be determined manually.

W. J. BAKER

2486. Determination of iron by ultra-violet spectrophotometry. R. Bastian, R. Weberling and F. Palilla (Sylvania Electric Products Co., Kew Gardens, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (4), 459-462.—A sensitive and accurate spectrophotometric procedure is described for the determination of 0.03 to 0.9 per cent. of Fe in a wide range of industrial alloys and glass samples. The extinction of Fe(ClO₄)₃ is measured at 240 or 260 m μ in a soln. containing ≈ 0.3 to 1.5 mg of Fe and 10 ml excess of HClO₄ per 100 ml. If Mn (> 5 mg) or Cr, or both, are present the soln. is boiled with 1 to 2 ml of 0.03 per cent. H₂O₂ and then cooled before making the measurement. Interfering ions are PO₄³⁻, NO₃⁻, Cl⁻ and F⁻ (F⁻ can be complexed with Al), but unless interference by Ni, Cu, V, Mo and Ti is appreciable most analyses can be made without their removal. The error is not usually $> \approx 0.1$ per cent.

W. J. BAKER

2487. Spectrophotometry of the ferrate ion in aqueous solution. Z. G. Kaufman and J. M. Schreyer (Kentucky Univ., Lexington, Kentucky, U.S.A.). *Chemist Analyst*, 1956, **45** (1), 22-23.—Solutions of K₂FeO₄ in 9 M KOH have been investigated spectrometrically 5 min. after the dissolution of the sample. The concn. decreases by ≈ 14 per cent. in the first 5 min. and then remains constant for as long as 60 min. The measurements are made at 25° C, a 1-cm cell and a 5-metre band-width being used. A linear relationship exists between concn. and extinction, giving a molar extinction index of 1.13×10^3 at 500 m μ where the max. extinction occurs.

J. H. WATON

2488. Simultaneous determination of ferrous and ferric ions by paper electrophoresis. F. Brom (Vysší škola pedagog., České Budějovice, Czechoslovakia). *Chem. Listy*, 1955, **49** (6), 938-940.—

Ferric and ferrous ions can be separated by electrophoresis on Whatman No. 1 paper soaked with 0.1 N H₂SO₄ after 90 min., with a potential drop of 10 V per cm. The respective mobilities at 18° C are 7.59×10^{-4} and 2.03×10^{-4} sq. cm per V per sec. The two zones are developed with K₃Fe(CN)₆ and 2:2'-dipyridyl, respectively.

G. GLASER

2489. Spectrophotometric determination of silicon and phosphorus in steel using stannous oxalate as reductant. C. O. Ingamells (4547 Chatham Rd., Minneapolis, Minn., U.S.A.). *Chemist Analyst*, 1956, **45** (1), 10-11.—A method is given by which Si and P can be determined in the same sample of steel with contents of Si and P of 0.05 to 0.50 per cent. and 0.001 to 0.050 per cent., respectively.

The determination can be carried out in the presence of Ti, Ta, Nb and W. Both elements are estimated as the reduction product of the respective heteropoly acids with Mo, stannous oxalate being employed as reductant because of the stability of its soln. and the reproducibility of its reducing action. *Procedure*—For the estimation of Si, a 10-ml aliquot of a soln. of the steel (prepn. described) is transferred to a 150-ml flask and diluted with 50 ml of H₂O, and 10 ml of ammonium molybdate soln. (100 g in 1900 ml of H₂O) are added. After being set aside for 5 min., the soln. is acidified with 20 ml of H₂SO₄ (5:15) and 10 ml of stannous oxalate (prepn. described) are added. The soln. is allowed to stand for at least 5 min., and its extinction is measured at 650 m μ against that of H₂O, 19-mm cells being used. For the estimation of P, a 25-ml aliquot is transferred to each of two 100-ml flasks. To one (sample), 10 ml of molybdate-formate soln. (prepn. described) are added, and to the other (blank) 10 ml of stannous oxalate reagent. Both soln. are allowed to stand for exactly 5 min. To the sample flask 10 ml of stannous oxalate reagent are added in one addition and the soln. is mixed immediately. To the blank flask 10 ml of molybdate-formate soln. are added. After 12 to 20 sec., 25 ml of NaF soln. (10 g per litre) are added to each flask. The extinction of the sample soln. is measured at 650 m μ against that of the blank in 25-mm cells. The colour begins to fade within 2 to 3 min. For both determinations, calibration curves are prepared from standard steels. Rubber stoppers must be avoided at all stages in the analysis, and Pyrex-glass apparatus (including pipettes) must be employed.

J. H. WATON

2490. Determination of silicon and phosphorus by photometry of their molybdc complexes. Application to the determination of silicon and phosphorus in steel. M. Jean. *Chim. Anal.*, 1956, **38** (2), 37-49.

—The various procedures for determining Si and P by spectrophotometry of their molybdenum complexes are evaluated critically and a detailed study is made of conditions affecting the formation, stability and composition of these complexes. The yellow molybdosilicic acid (I) formed at pH 1.5 to 2 always has a ratio of MoO₃ to SiO₂ of 12, the β -acid first formed slowly transforming into the α -acid with diminished colour intensity. The β to α conversion, which is accelerated by increasing temp., time or pH, is confirmed by polarography, complete formation of the α -acid corresponding to the max. on the polarogram. The facts do not suggest hydrolysis, decomposition or a colourless form of I. The measurement of extinction at 405 m μ should be made ≈ 20 to 45 min. after the prep. of the coloured soln. When Si is determined as the molybdenum-blue complex, the acidity of the soln.

should be raised to $\approx 2N$ before the reducing agent is added, otherwise P and As interfere. The ratio of MoO_3 to P_2O_5 in the molybdophosphoric acid formed in $\approx N$ H_2SO_4 soln. is always 12. When P is determined as the molybdenum-blue complex, the concn. of MoO_3 in the final soln. should be ≈ 120 mg per 100 ml; 1 per cent. aq. ascorbic acid is preferable to hydrazine as reducing agent, and the colour should be developed at 100°C (steam-bath) for exactly 5 min. These methods can be applied directly to the photometric determination of Si and P in steel after dissolution of the sample in an acid mixture and reduction of the cool diluted soln. with NaHSO_3 . A standard procedure for determining P (as the molybdenum-blue complex) in stainless and other steel is described fully. There is no interference by As. W. J. BAKER

2491. Mixed perchloric-phosphoric acids as solvents for iron ores. C. A. Goetz and E. P. Wadsworth, jun. (Dept. of Chem., Iowa State Coll., Ames, U.S.A.). *Anal. Chem.*, 1956, **28** (3), 375-376.—A mixture of equal vol. of HClO_4 (72 per cent.) and of H_3PO_4 (85 per cent.) rapidly dissolves iron ores, and is superior to HCl . It can be used in a rapid method for estimating Fe. *Procedure*—To the weighed sample (0.3 to 0.35 g) are added ≈ 20 ml of the acid mixture and the acids are heated gently under reflux to boiling point. The sample dissolves in ≈ 10 min., after which the flask is cooled a little and the soln. is diluted with 70 ml of H_2O . The soln. is boiled for ≈ 2 min. to expel Cl_2 , then cooled, and ≈ 30 ml of H_2SO_4 (1:1) are added. The Fe is reduced by passing the soln. through a Jones reductor at a rate of ≈ 50 to 60 ml per min. into a receiving flask containing ≈ 0.2 g of Na_2CO_3 . The soln. is washed through the column with H_2SO_4 (1:20) (3×25 ml) and finally with H_2O (3×25 ml). The Fe^{2+} are titrated with standard KMnO_4 or $\text{Ce}(\text{SO}_4)_2$ soln., with ferroin as indicator. With $\text{Ce}(\text{SO}_4)_2$, rapid stirring is necessary to prevent the pptn. of insol. ceric phosphate. J. H. WATON

2492. Deliberate sampling of iron minerals. M. D. E. Jonckers (S. A. Forges de la Providence, Marchienne-au-Point, Belgium). *Chim. Anal.*, 1955, **37** (11), 359-367.—The deliberate sampling of material by hand as opposed to sampling by chance is considered, and an example is given to compare the results of the two methods. The theoretical laws underlying sampling are discussed, as well as the reduction of the sample, for which a scheme is given. J. H. WATON

2493. The determination of cobalt in high alloyed steels and magnet alloys. F. Cassy (Darwins Ltd., Tinsley, Sheffield). *Chem. & Ind.*, 1956, (16), 305-307.—The Co, previously separated from Mn and Cr, is pptd. by means of phenylthiohydantoic acid. The ppt. is decomposed with H_2SO_4 and HNO_3 and determined potentiometrically by adding an excess of standard $\text{K}_3\text{Fe}(\text{CN})_6$ and back-titrating with cobalt soln. O. M. WHITTON

2494. Amperometric titration of cobalt with anthranilic acid. A. K. Zhdanov and A. M. Yakubov. *Trudy Sredneaziat. Gosudarst. Univ. (Tashkent), Khim. Nauk.*, 1954, **55** (7), 71-75; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,114.—Cobalt (30 to 63 mg in 50 ml) in 0.05 M Na acetate or soln. of KNO_3 , KCl , KSCN , Na_2SO_4 or MgSO_4 containing 15 per cent. of ethanol is titrated amperometrically at pH 4.5 to 7.5 with 0.17 M Na anthranilate, a dropping-mercury electrode being used. Magnesium

(24 to 486 mg), Al (> 0.1 mole per litre) and Cr (≈ 0.04 mole per litre) do not interfere. G. S. SMITH

2495. Polarographic determination of cobalt in presence of nickel. L. Meites (Polytech. Inst. Brooklyn, 99 Livingston St., Brooklyn, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 404-406.—The polarographic method of Kolthoff and Watters has been modified and shortened by substituting KMnO_4 for sodium perborate. The oxidation is carried out in the presence of aq. NH_3 and NH_4Cl , and the excess of reagent is destroyed with hydroxylamine sulphate. After removal of air from the soln., the polarogram is recorded from -0.2 to -0.8 V vs. the S.C.E.; the E_1 for the reduction of Co^{III} is ≈ -0.4 V. The final soln. should be ≈ 0.5 M in NH_4Cl and M in aq. NH_3 . No interference occurs with As, Cd, Sb, Sn and Zn, whilst Bi, Cu, Fe, Mn and Mo can be tolerated in moderate amounts. Relatively large amounts of Cr or Pb are handled by the introduction of an excess of either BaCl_2 or Na_2SO_4 , respectively; W and V must be absent. In the analysis of a nickel salt with a cobalt content of ≈ 0.1 per cent., the results show a standard deviation of ± 2.6 per cent. J. H. WATON

2496. Determination of heavy metals by means of EDTA. I. Titration of EDTA with cobaltous solution. Susumu Takamoto (Faculty of Sci., Gakushuin Univ., Toshima-ku, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (12), 1339-1342.—A search to find a suitable indicator for the titration of EDTA with CoCl_2 was made and a mixture of KSCN (saturated aq. soln.) and acetone (4 + 20 by vol.) was found to be the best for a titration with 0.01 to 0.05 M soln. At the end-point the pale-rose colour changes to rose-purple and then to blue with excess of Co^{2+} . When the titration is carried out in ammonium acetate soln. (6 N, 3 ml for 35 ml of the sample soln.), the presence of acids or bases in concn. $< 2N$ does not vitiate the result.

II. Titrations of various metals using thiocyanate-acetone as indicator. Susuma Takamoto. *Ibid.*, 1955, **76** (12), 1342-1344.—Aqueous soln. of various heavy metals, including Fe^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} and Sn^{2+} , are treated with EDTA (disodium salt) in ammonium acetate and the excess of EDTA is titrated with Co^{2+} , with a mixture of KSCN and acetone as indicator. The stability of the EDTA complex of Co^{2+} is so increased under the given conditions that the EDTA complexes of some metals (Pb, Zn, Cd, etc.) are decomposed by the addition of Co^{2+} . The indicator should be added after complex formation between EDTA and the ions of the metal is completed.

III. Titration of various rare metals. Susumu Takamoto. *Ibid.*, 1955, **76** (12), 1344-1345.—The work was extended to some rare metals, including lanthanides, Be, Ga, Ti^{3+} , Zr and Th. Thallium and UO_2^{2+} fail to produce EDTA complexes under the given conditions. Metals can be determined only in the absence of other metal ions capable of forming a complex with EDTA. K. SAITO

2497. Amperometric titration of nickel with anthranilic acid. A. K. Zhdanov and A. M. Yakubov. *Trudy Sredneaziat. Gosudarst. Univ. (Tashkent), Khim. Nauk.*, 1954, **55** (7), 65-69; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,113.—Nickel (20 to 60 mg in 50 ml) in soln. of KNO_3 , KCl , Na_2SO_4 , MgSO_4 or Na acetate containing 15 per cent. of

ethanol is titrated amperometrically at pH 3 to 7 and at -1.6 V with 0.17 M Na anthranilate having a pH of 5.4. Magnesium sulphate (24 to 486 mg), Al (> 0.1 mole per litre) and Cr (> 0.04 mole per litre) do not interfere. G. S. SMITH

2498. Gravimetric determination of palladium (II) and mercury (II) as bis(ethylenediamine)palladium (II) tetraiodomercurate (II). G. W. Watt, D. M. Sowards and R. E. McCarley (Univ. of Texas, Austin, Tex., U.S.A.). *Anal. Chem.*, 1956, **28** (4), 556.—A procedure for the quantitative determination of milligram amounts of Hg^{++} or Pd^{++} as bis(ethylenediamine)palladium^{II} tetraiodomercurate^{II} [$\text{Pd}(\text{en})_2\text{HgI}_4$] at pH 6 to 8 is described. An excess of a soln. of potassium tetraiodomercurate^{II} (≈ 0.9 M HgI_4) is added dropwise to the sample soln., and after 10 min. the ppt. is filtered off on a fritted-glass crucible, washed with H_2O and dried to const. wt. at 115°C . Most common anions do not interfere. X-ray diffraction data for $\text{Pd}(\text{en})_2\text{HgI}_4$ are listed. W. J. BAKER

See also Abstracts 2382, 2383, 2385, 2386, 2390, 2391, 2571, 2578, 2585, 2596, 2599.

3.—ORGANIC ANALYSIS

2499. Open absorption tubes for semi-micro determination of carbon and hydrogen. J. Körbl (Výzkumný ústav pro farm. a biochem., Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (6), 929-931.—A thin-walled glass tube (10 mm in diameter), drawn out and sealed at one end, is filled with the required absorbent (kept in position by a plug of cotton wool) and closed by drawing out and sealing the other end. Before use the tapered ends are cut off. The tube is disposed of after exhaustion, thus obviating difficulties encountered in the cleaning and refilling of absorption tubes of current design. The tube is handled by means of a special steel-spring holder with rubber cushions, which closes both ends and prevents diffusion between the inside of the tube and the atmosphere.

G. GLASER

2500. Organic elementary micro-analysis. I. Improvement of the method of supplying carbon dioxide for the micro Dumas nitrogen determination. Minoru Inada (Pharm. Inst., Univ. of Osaka, Hotarugaike, Toyonaka, Osaka). *J. Pharm. Soc. Japan*, 1955, **75** (2), 151-153.—A modification in the apparatus for CO_2 generation for the micro Dumas method was suggested with the object of obtaining a constant flow of CO_2 . The water resulting from pyrolysis of NaHCO_3 is removed through a trap attached to the CO_2 container. The rate of flow is easily adjusted by regulating the pressure with the aid of a new type of stop-cock. This apparatus consumes about 45 g of NaHCO_3 when used for 9 hr. K. SAITO

2501. Micro-determination of acetyl and benzoyl groups by means of cation-exchange resin. Hideo Tani and Akio Nara (Kofuku Sangyo Co., Ltd., Shimo-takaido, Suginami-ku, Tokyo). *J. Pharm. Soc. Japan*, 1954, **74** (12), 1399.—Organic compounds (4 to 10 mg) containing acetyl or benzoyl groups are saponified with a mixture of NaOH (5 N, 1 ml) and ethanol (2 ml) on a water bath. The product is mixed with water and passed through a column of Amberlite IR-120 (H). The eluate and the washings, consisting of pure acetic or benzoic acid, are boiled for 20 sec. and titrated with NaOH (0.01 N); the error is < 0.5 per cent. K. SAITO

2502. A new solvent for quantitative paper chromatography of sugars. G. Giovannozzi-Sermanni (Ist. Sci. Sper. Tabacchi, Rome). *Nature*, 1956, **177**, 586-587.—The solvent mixture employed for the separation of seven sugars comprises n-propanol, benzyl alcohol, water and 85 per cent. formic acid (50:72:20:20 by vol.). At 20°C the following R_F values were obtained: sucrose, 0.17; glucose, 0.26; mannose, 0.30; arabinose, 0.32; fructose, 0.32; xylose, 0.33; ribose, 0.41. The separation of sucrose, fructose and glucose is sufficiently good to eliminate errors in the computation of common areas. Photometric readings with this solvent give a graph of well-separated curves. D. G. HIGGS

2503. EDTA procedure for volumetric determination of reducing sugars. H. Eschmann (Cantonal Lab., Berne, Switzerland). *Chemist Analyst*, 1956, **45** (1), 5-6.—EDTA is superior to citric and tartaric acids for stabilising alkaline soln. of Cu in the estimation of reducing sugars. An alkaline Cu-EDTA soln. is prepared which contains 37.22 g of EDTA (disodium salt), 286 g of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and 25 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per litre. This soln. (10 ml) is refluxed for 10 min. with 10 ml of the sugar soln. (containing 2.5 to 35 mg). The resulting ppt. of Cu_2O is dissolved in 5 to 10 ml of M HNO_3 , and the soln. is made ammoniacal with ≈ 20 ml of M aq. NH_3 and diluted with 100 ml of H_2O . After 10 to 30 mg of murexide indicator powder have been added, the Cu is titrated with 0.02 M EDTA. Empirical factors are given for the calculation of glucose, fructose, lactose and maltose from the vol. of EDTA used.

J. H. WATON

2504. Chelatometry. V. The decomposition product of Bindschedler's green as redox indicator. 2. Determination of ethylenediaminetetra-acetic acid (EDTA) with ferric salt. P. Wehber (Metallhütte Mark A.-G., Hamburg-Wilhelmsburg, Germany). *Z. anal. Chem.*, 1956, **149** (4), 241-244.—The EDTA in technical prep. containing various amounts of Ca, Si, Mg, Ba and Al is best determined in acid soln. (pH 2.5 to 3.5) by titration with FeCl_3 , the decomp. product of Bindschedler's green (cf. *Anal. Abstr.*, 1956, **3**, 2088) being a useful indicator. Reproducibility on ≈ 40 per cent. EDTA in commercial products is within ± 0.2 per cent. *Procedure*—Dissolve the sample of EDTA in H_2O (60 to 70 ml) at 17° to 26°C . Add 10 ml of buffer soln. and the mixed indicator (80 mg) and titrate with 0.1 M FeCl_3 to a green end-point. The exact colour at the end-point depends on the composition of the mixed indicator.

J. P. STERN

2505. Photometric method for the determination of small amounts of thiophen in benzene. J. Kolšek, M. Perpar and A. Rauschl (Inst. Org. Chem., Ljubljana Univ., Yugoslavia). *Z. anal. Chem.*, 1956, **149** (5), 321-325.—Thiophen in purified benzene is determined photometrically by reaction with van Urk's reagent [*p*-dimethylaminobenzaldehyde (I) in aq. H_2SO_4 containing a little FeCl_3]. The optimum sensitivity is 0.4 mg per ml, and 0.01 mg per ml can be readily determined. The method is unsuitable for crude benzene, as other impurities interfere. *Procedure*—To the diluted benzene sample (3 ml) in a separating funnel add the reagent (4 ml of a soln. of 0.1 g of I in 72 ml of conc. H_2SO_4 and 28 ml of water containing 0.19 ml of 5 per cent. FeCl_3). Shake the soln. for exactly

10 min., dilute immediately with water (10 ml), and set aside for 5 min. Determine the extinction, at 552 m μ , of the lower (aq.) phase in the twentieth minute and compare with a blank. J. P. STERN

2506. Determination of cyclopentadiene in liquid and gaseous mixtures. M. Vraný and M. Bohdanecký (Výzkumný ústav synth. pryskyřic, Pardubice, Czechoslovakia). *Chem. Listy*, 1955, **49** (6), 936-938.—The photometric method of Uhrig *et al.* (*Brit. Abstr. C*, 1946, 251), based on the formation of coloured fulvenes from cyclopentadiene (I) and aldehydes in alkaline media, has been improved. To determine I in liquid mixtures, dilute the sample (1 to 5 ml) to 50 ml with light petroleum (boiling range, 160° to 210° C), transfer a 5-ml aliquot to a depolymerisation apparatus of special design (illustrated) and dilute it with light petroleum (5 ml, boiling range, 40° to 60° C). Evaporate the soln. at 170° to 210° C, collect the depolymerised I in a mixture of a 20 per cent. ethanolic soln. of benzaldehyde (5 ml) and 3 per cent. ethanolic KOH (5 ml), flush the apparatus by evaporating light petroleum (5 ml) to dryness, and wash down the apparatus with ethanol (5 ml). Acidify the absorption mixture with acetic acid (1 ml), dilute it to 50 ml with benzene and compare the extinction with a blank carried out with 5 ml of the high-boiling light petroleum. The determination of I in gases is carried out by absorbing the gases, freed from H₂S by passage through soda-lime, in two absorption tubes, the first containing 10 ml of ethanolic benzaldehyde, 10 ml of ethanolic KOH and 20 ml of benzene, and the second 10 ml of benzene with equal amounts of the benzaldehyde and KOH soln. G. GLASER

2507. Determination of 4-ethylpyridine. A. Kolusheva and N. Nin'ov. *Farmatsiya (Sophia)*, 1954, (3), 19-22; *Ref. Zhur., Khim.*, 1955, Abstr. No. 29,258.—The method is based on the oxidation of 4-ethylpyridine to isonicotinic acid with K₂Cr₂O₇ and determination of the excess of oxidising agent. The sample (0.07 to 0.10 g) is treated with 10 ml of a K₂Cr₂O₇ soln. (75 g of K₂Cr₂O₇ dissolved in 100 ml of conc. H₂SO₄, diluted to 1000 ml with water) and 10 ml of conc. H₂SO₄. After 1 hr., 600 to 700 ml of water, 2.5 ml of conc. H₃PO₄, 5 to 8 drops of a diphenylamine soln. (0.5 g in 100 ml of conc. H₂SO₄ and 20 ml of water) are added, and the excess of K₂Cr₂O₇ is titrated with a soln. of ferrous ammonium sulphate (200 g and 50 ml of conc. H₂SO₄ in 1000 ml of water) to a green end-point. The error is \pm 0.5 per cent. An iodimetric titration can also be used. The oxidised mixture is diluted with water to a vol. of 600 to 700 ml, 3 g of KI are added, and the liberated I is titrated after 2 min. with N Na₂S₂O₃. The error is 3 per cent. The method is applied to the determination of 4-ethylpyridine in the manufacture of isoniazid. G. S. SMITH

2508. Gas chromatography. Analysis of gaseous hydrocarbons by gas-liquid partition chromatography. E. M. Fredericks and F. R. Brooks (Shell Dev. Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 297-303.—The application of gas chromatography to the quant. analysis of complex hydrocarbon mixtures is described. Most hydrocarbons up to C₆ can be resolved by a two-stage column in which the sample is partitioned first by a column (6 ft.) of disodecyl phthalate and then by a column (22 ft.) of dimethylsulpholane (tetrahydro-2:4-dimethylthiophen-5-dioxide). But-2-ene can be separated from but-1-ene with a

column (50 ft.) of dimethylsulpholane; the pentenes can also be resolved by this column. Thermal-conductivity detection is used, with He as the carrier gas. A quant. measure of composition is obtained from the areas under the peaks of the recorded curves. Qualitative separation and identification of the commonly encountered hydrocarbons can be achieved by this method.

K. A. PROCTOR

2509. Gas chromatography. Use of liquid-modified solid adsorbent to resolve C₅ and C₆ saturates. F. T. Eggertsen, H. S. Knight and S. Groennings (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 303-306.—A new type of column packing for gas chromatography, consisting of an active solid (Pelletex, a commercial carbon black) with a small amount of liquid solvent (1.5 per cent. of squalane, 2:6:10:15:19:23-hexamethyltetracosane) is described. Ten commonly encountered C₅ and C₆ saturated hydrocarbons were separated on a column (50 ft.) in about 2 hr. with an average error of 0.5 per cent. The composition was obtained by measuring the areas under the peaks. The added solvent greatly reduces the tailing of peaks that is normally encountered, and such a liquid-modified adsorbent resembles unmodified solids in retaining paraffins relative to naphthenes. The C₅ naphthenes thus emerge before the C₆ paraffins, in contrast to their behaviour in gas-liquid columns. Peak separation becomes poorer with increasing sample size and temp., so that $>$ 20 mg of sample or 3 mg of similar components should be used with a temp. of 40° C or less.

K. A. PROCTOR

2510. White spirit. British Standards Institution (2 Park St., London). B.S. 245:1956, 36 pp.—This revised standard includes more extensive requirements for the superior quality spirit now being produced for uses other than those in the paint industry. The standard distillation apparatus and the distilling range are slightly modified. A new flash-point of \leq 93° C is laid down. There are new specifications for the determination of colour, aromatic content, residue on evaporation, and freedom from objectionable sulphur compounds. In each case, Institute of Petroleum methods have been adopted and are detailed in appendices. Provision is also made for routine checks of distillation requirements, residue on evaporation, and flash-point. D. G. FORBES

2511. Spectrophotometric determination of carbonyl sulphide in petroleum refinery gases. F. J. O'Hara, W. M. Keely and H. W. Fleming (The Girdler Co., Louisville, Ky., U.S.A.). *Anal. Chem.*, 1956, **28** (4), 466-470.—The procedure described depends on the reaction (during 40 to 80 min.) of COS in 0.043 per cent. aq. soln. of piperidine to form quant. piperidinium pentamethylenethiocarbamate, the max. u.v. extinction of which is measured at 230 m μ in a 1-cm cell. The pH of the aq. piperidine soln. must be kept at 11.2 \pm 0.2 during the extraction. There is no interference from H, O, N, CO, CH₄, C₂H₆, C₂H₂, C₃H₈, C₃H₄ and C₄H₆, but H₂S, methanethiol, CO₂ and SO₂ should be initially removed by washing the sample with Shaw's reagent [a mixture (1 + 7, by vol.) of N Na₂CO₃ and aq. 10 per cent. CdCl₂] and aq. 30 per cent. NaOH. Interference by CS₂, thiophen and 1:3-butadiene, etc., is corrected by running a blank and subtracting its extinction from that for the first extraction. In the absence

of interfering components, or where a blank correction is made, the accuracy is within 1 p.p.m. over the range 1 to 50 p.p.m., but where a washing train is used the error can be up to 10 per cent. because of hydrolysis of COS.

W. J. BAKER

2512. Schütz - Unterzaucher method for the direct determination of oxygen in coal. J. G. King. *Coke & Gas*, 1956, **18**, 31-32.—The Schütz method of determining O in organic substances consists in heating the material with active C in a stream of pure N at 1120° C, whereby the O is converted quant. into CO, which is then oxidised to CO₂ by either HgO (150° to 250° C) or I₂O₅ (120° C). The CO₂ is determined by absorption in 0.05 N Ba(OH)₂ or by titration of liberated I with 0.02 N Na₂S₂O₃ (Schütz, *Anal. Chem.*, 1939, **118**, 241). The accuracy of the method and its application to coal are discussed.

S.C.I. ABSTR.

2513. Ion-exchange chromatography of coal tar and pitch. J. D. Brooks (Coal Res. Sect., C.S.I.R.O., Sydney, Australia). *Chem. & Ind.*, 1956, (16), 316-317.—The Zeo-Karb 225 (I) and De-Acidite FF (II) resins used were regenerated with aqueous soln. and then equilibrated while wet with a mixture of ethanol, benzene and water (57:40:3). To a filtered soln. of tar or pitch in benzene, sufficient ethanol was added to bring the solvent to the composition given above. After passage first through I and then through II, washing in each case with the solvent mixture until the soln. was no longer coloured, the combined soln. were evaporated to obtain the neutral oil fraction. The bases were eluted from I with a mixture of ethanol, benzene and 5 N HCl (57:37:6) and the HCl was then removed from the soln. of the bases by passage through a column of freshly conditioned II. The phenols were eluted from II with a mixture of ethanol, benzene and 8 N NaOH, the NaOH then being removed from the eluate by passage through I. Results are compared with those obtained by extraction.

O. M. WHITTON

2514. Refractometric estimation of the fat content of raw wool. G. Nitsche (Res. Inst. Textile Technol., Leipzig). *Faserforsch. u. Textiltech.*, 1955, **6** (12), 566-568.—Tables are given for enabling the fat content of raw wool to be fixed from determinations of solutions of the extracted fats in 10 ml of ether. The data are obtained from estimations in which the fat content is determined by Soxhlet extraction of the raw wool with light petroleum, subsequent evaporation of the solvent and drying the extracts to constant wt.; the dried extracts are then dissolved in 10 ml of ether and the refractive indices of the ether solutions are measured. Correcting factors are worked out for the variation in constitution, and hence of refractive index of the fats, of wools of different geographical origins. Practical tests prove this method to be sufficiently accurate for rapid control work (the general accuracy is within ± 10 per cent. and the max. error is ± 20 per cent.), and to be far more rapid than the lengthy method of Soxhlet extraction and drying the extract to constant wt.

H. L. WHITEHEAD

2515. Amperometric titration of viscose. M. Wronski (Univ. Łódź, Poland). *J. Polymer Sci.*, 1956, **19**, 213-214.—Amperometric titration gives better precision and is quicker than potentiometric in investigations of viscose. For titration of Na₂S, Na₂S + Na₂CS₃, or Na₂CS₃, 0.04 N Pb(NO₃)₂ soln.

in the presence of 0.1 N NaOH soln. is recommended. Sodium sulphite, thiosulphate and xanthate do not interfere.

B. J. WALBY

2516. Chromatography of dyestuffs intermediates. IV. Paper chromatography of dinitrotoluenes, dinitronaphthalenes and dinitroanthraquinones. J. Franc (Výzkumný ústav org. syntesy, Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1955, **49** (6), 872-875.—The conditions for the chromatographic separation of a number of aromatic dinitro compounds were studied. Good separation was achieved by descending chromatography on Whatman No. 4 paper impregnated with paraffin (boiling range 190° to 275° C), a mixture of 96 per cent. ethanol, water and acetic acid (20:14:1) being used as the mobile phase. The spots were detected either by spraying with Ehrlich reagent or, under u.v. light, after being sprayed with 0.005 per cent. ethanolic fluorescein. The R_F values of the individual compounds at 24° \pm 1° C were as follows—*o*-dinitrobenzene, 0.76; *m*-dinitrobenzene, 0.56; 1-nitronaphthalene, 0.33; 1:5-dinitronaphthalene, 0.00; 1:8-dinitronaphthalene, 0.80; 1-nitroanthraquinone, 0.17; 1:5-dinitroanthraquinone, 0.00; 1:8-dinitroanthraquinone, 0.77; 1:6-dinitroanthraquinone, 0.43; 1:7-dinitroanthraquinone, 0.70; anthraquinone, 0.28. With the exception of *o*-dinitrobenzene, the experimental R_F values were in good agreement with those calculated from the equation $R_F = K + 0.1 \mu$, where μ is the dipole moment.

G. GLASER

2517. Analysis of nail lacquers. II. Separation of nitrocellulose from pigments. S. H. Newburger (Div. Cosmetics, Food and Drug Admin., Dept. Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (1), 259-260.—The pptd. nitrocellulose and pigments (*Anal. Abstr.*, 1956, **3**, 162), dissolved and dispersed with 25 ml of hot ethyl methyl ketone, and then treated with 4 drops of water and 50 mg of silicic acid, are centrifuged. The residue after decantation is treated with 15- and 10-ml portions of the ketone and centrifuged after each treatment. The combined supernatant liquids, separated after shaking with dil. HCl, are extracted with dil. aq. NH₃-NH₄Cl soln. saturated with the ketone. The ketone soln., after again being washed with dil. HCl, is filtered and evaporated under specified conditions to afford nitrocellulose.

A. A. ELDRIDGE

2518. Analysis of styrenated methyl esters of linseed-oil fatty acids by molecular distillation. S. S. Tiong, H. I. Waterman and C. Boelhouwer (Delft Univ., Holland). *Anal. Chim. Acta*, 1956, **14** (3), 228-234.—The distillation of the reaction products (clear oils) of methyl esters of linseed-oil fatty acids with gaseous styrene at 280° C can be effected successfully in a cascade fractionating molecular still having nine stages of vaporisation and condensation. The design and operation of the still are described, and the physical properties of each of the 27 fractions obtained between 120° and 254° C are listed. The values of n_D^{20} indicate chemical combination between styrene and esters.

W. J. BAKER

2519. Determination of butoxyl groups in butanol-modified phenolic resins. Z. Ditrych, H. Rejchová and V. Ulbrich (Výzkumný ústav synth. pryskyřic, Pardubice, Czechoslovakia). *Chem. Listy*, 1955, **49** (6), 869-871.—The existing methods for the

semi-micro determination of butoxyl groups in butanol-modified phenolic resins have been re-examined and the Zeisel method, carried out under the following conditions, was found to be best—heating-bath temp. 175° C, cooling-water temp. 40° C, reaction time 3 hr. from the time the hydriodic acid begins to boil, and titration with 0.02 or 0.05 N Na₂S₂O₃. Butyl phenylcarbamate is used for standardisation. G. GLASER

2520. Polarographic determination of quinol in monomers. J. Exner and M. Bohdanecký (Výzkumný ústav synth. pryskyřic, Pardubice, Czechoslovakia). *Chem. Listy*, 1955, **49** (7), 1091-1093.—Quinol in neutral vinyl monomers can be determined polarographically vs. a graphite electrode, with a mean error of ± 2 per cent. The monomer is dissolved in a mixture of methanol and benzene containing 0.1 M ammonium acetate as electrolyte. The well-defined diffusion wave has a $E_{1/2}$ of + 0.05 V, its height being proportional to quinol concn. G. GLASER

2521. Determination of the monomer in poly(methyl methacrylate). Yuji Takayama (Mitsubishi Rayon Co. Ltd., Kyobashi, Tokyo). *Japan Analyst*, 1955, **4** (10), 634-636.—The extinction of the aq. soln. of monomeric methyl methacrylate (I) at 250 m μ is proportional to concn. in the range 0.005 to 0.04 ml per 20 ml. The sample of poly(methyl methacrylate) is dissolved in glacial acetic acid (20 ml) and distilled with water (20 ml) to collect all the I and a small amount of acetic acid in the distillate (20 ml), the extinction of the latter being measured at 250 and 260 m μ . The acetic acid, which shows a similar absorption, is titrated with 0.5 N NaOH and the measured extinctions are calibrated. When the distillate consists of only I and acetic acid, the ratio of extinction coeff. at 250 m μ to that at 260 m μ is 3.29, indicating that this method is practicable. No interference is given by benzoyl peroxide, and results compare favourably with those obtained by the polarographic or colorimetric method. K. SAITO

2522. Estimation of water in polyamide chips by the Karl Fischer method. H. Reimschuessel (Lab. H. J. Zimmer Processtechnique, Frankfurt, Germany). *Faserforsch. u. Textiltech.*, 1955, **6** (12), 568.—Better results are said to be obtained by following the technique given below instead of that proposed by Sieber (*cf. Anal. Abstr.*, 1956, **3**, 1807). The amount of methanol to be used as extracting agent is first titrated to the end-point change with Karl Fischer reagent in an Erlenmeyer flask. The weighed sample of chips is then introduced into the titrated solution and allowed to stand, with occasional swirling, for the requisite time (1 hr. to a max. of 3 hr.), after which the solution is titrated by the usual method, preferably with electrometric indication. H. L. WHITEHEAD

2523. Determination of the hardness of paint [films]. P. Crovetto. *Pitt. e Vern.*, 1955, **11** (10), 651-657.—Hardness meters based on a penetration, oscillation or scratch principle are compared. A critical review of the oscillation type is made and figures obtained for different types of paint are tabulated. The principal errors with this method are considered to be caused by inadequate control of temp. and humidity, the test panel not being perfectly plane and immobile, surface irregularities in the film, and imperfect polishing of the metal rocker. L. A. O'NEILL

See also Abstracts 2453, 2583.

4.—BIOCHEMISTRY INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

2524. The measurement of consistency of some biological fluids using a new micro-consistometer. G. W. Scott Blair and F. A. Glover (National Inst. for Research in Dairying, Shinfield, Reading). *Lab. Practice*, 1956, **5** (4), 125-128.—A pocket-sized 'consistometer' is described in which a measured pressure is applied to ≈ 0.01 to 0.001 ml of the subject liquid in an emptying capillary. For Newtonian liquids the ordinary theory of emptying capillaries applies and η is given by the slope of the straight-line plot of t (time in sec.) against $L^2 - l^2$, where L is the original length of the liquid and l is the length of the shortening column after t sec. The instrument described is not as accurate as conventional viscometers for Newtonian liquids, but for biological liquids it is able to measure sufficiently accurately the 'quasi-property' involved. Thus for cervical secretions the function Pt^k is found to be independent of P (where P is the pressure applied), and a similar 'quasi-property' involving a fractional power of t can be found for other substances. For the fluids considered, temp. control is not necessary, but could easily be provided for. The instrument can also be used to measure flow-elasticity by measuring the recoil of the liquid in the capillary on releasing the pressure. The results of the consistometer for a syrup when compared with other methods are discussed, and some negative thixotropy is postulated to explain the observed differences, though the syrup is rheologically much simpler than the biological fluids considered. E. J. H. BIRCH

2525. A new method of serum-iron determination and commentary on various methods of determination. Takakata Matsubara (Univ. Coll. Med., Kumamoto, Japan). *Kumamoto Med. J.*, 1955, **8** (2), 81-92.—To 2 ml of serum in a 15-ml tube add 2.0 ml of N HCl, stir well and keep at 37° C overnight. Add 1.0 ml of 30 per cent. trichloroacetic acid, mix and keep at 37° C for 30 min. Centrifuge at 3000 r.p.m. for about 10 min. and transfer 2.5 ml of supernatant to a test-tube graduated at 10.0 ml. Add 1 drop of 1 per cent. soln. of *p*-nitrophenol in ethanol and then aq. NH₃ dropwise until a yellow coloration is obtained; add 1.0 ml of *o*-phenanthroline hydrochloride (I) or 2:2'-dipyridyl (II) soln. (0.1 per cent. in 2 M sodium acetate-acetic acid buffer of pH 3.8) and 0.5 ml of 2 per cent. hydroxylamine hydrochloride. Dilute to 10 ml, keep at 37° C overnight and measure the extinction at 510 m μ for I or 521 m μ for II. Prepare a standard curve covering the range 1 to 10 μ g of Fe and a reagent blank by omitting the serum. The advantages claimed for this method are good recovery of iron, negligible effect of haemolysis, and little danger of contamination. H. F. W. KIRKPATRICK

2526. Quantitative estimation of haemoglobin, oxyhaemoglobin, carboxyhaemoglobin and methaemoglobin in small blood samples by means of spectrophotometry. W. G. Zijlstra (Lab. physiol. Chemie, Reichsuniv., Groningen, Holland). *Klin. Wochschr.*, 1956, **34** (13-14), 384-389.—Procedures are described for the following determinations: (1) total haemoglobin, by conversion into cyanmethaemoglobin by treatment of the blood with

$K_3Fe(CN)_6$ and NaCN and measuring the extinction at 540, 545 and 551 $m\mu$; (2) oxyhaemoglobin (I) in mixture with reduced haemoglobin by measuring the extinction at 560 and 506 $m\mu$; (3) carboxyhaemoglobin in mixture with I by measuring the extinction at 562 and 540 $m\mu$; (4) methaemoglobin in mixture with I in 0.1 per cent. aq. NH_3 soln. by measuring the extinction at 540 and 524 $m\mu$.

H. F. W. KIRKPATRICK

2527. Inhibition of colour development in the Lowry-Lopez phosphorus method by sulphhydryl compounds and its counteraction by copper. J. H. Bruemmer and B. L. O'Dell (Dept. of Agric. Chem., Univ. of Missouri, Columbia, Mo., U.S.A.). *J. Biol. Chem.*, 1956, **219** (1), 283-286.—Glutathione and cysteine delay the rate of colour development in the determination of inorg. $PO_4^{'''}$ by the method of Lowry and Lopez (*Brit. Abstr. C*, 1946, 286). This effect is annulled by the addition of $CuSO_4$, which also eliminates the effect of other inhibitors present in tissue extracts.

J. N. ASHLEY

2528. The occurrence and determination of δ -aminolaevulinic acid and porphobilinogen in urine. D. Mauzerall and S. Granick (Rockefeller Inst. for Med. Res., New York, U.S.A.). *J. Biol. Chem.*, 1956, **219** (1), 435-446.—Colorimetric methods are described for the determination of δ -aminolaevulinic acid and porphobilinogen in urine. The sample is passed through a column of Dowex-2 resin in the acetate form, which holds back the porphobilinogen while the δ -aminolaevulinic acid and urea are eluted from it with water. The porphobilinogen is then eluted with acetic acid and is determined spectrophotometrically at 555 $m\mu$ after condensation with Ehrlich reagent. The aqueous washings from the Dowex-2 column are passed through a column of Dowex-50 resin in the acid form; the urea is then washed out with water, and the δ -aminolaevulinic acid is eluted with aqueous sodium acetate and treated with acetylacetone at pH 4.6. The resulting pyrrole is determined spectrophotometrically at 553 $m\mu$ after reaction with a modified Ehrlich reagent. The error in both methods is < 5 per cent. and the limit of detection (extinction of 0.01 for a 1-cm light path) in 1 ml of urine is 1 μg for porphobilinogen and 0.5 μg for δ -aminolaevulinic acid.

J. N. ASHLEY

2529. The absorption spectra of bile acids in sulphuric acid. S. Eriksson and J. Sjövall (Dept. Physiol. Chem., Univ. Lund, Sweden). *Ark. Kemi*, 1955, **8** (4), 303-310.—The absorption spectra of unconjugated bile acids in conc. and 65 per cent. H_2SO_4 are described. For quant. determination the use of 65 per cent. H_2SO_4 is preferred. Standard soln. of 1 mg of bile acid per ml of ethanol were prepared and 20-ml aliquots were transferred to small test-tubes, each having a cap with an outlet tube bent downwards. The alcohol was removed by placing the tubes in an air oven at 100° C for about 4 hr.; 1 ml of 65 per cent. H_2SO_4 was added to each cooled tube and the tubes were shaken until all of the bile acid had dissolved. Cholic acid samples were heated for 15 min. and dihydroxy acids for 60 min. at 60° C. After being cooled, the tubes were allowed to stand at room temp. for 15 min., then the cholic acid was measured at 320 $m\mu$ and the dihydroxy acids at 385 $m\mu$. Glass-distilled water is essential for making the 65 per cent. H_2SO_4 as traces of iron completely alter the absorption curves. Ether peroxides have a similar effect so that isopropyl ether cannot be used as solvent for

separating the bile acids chromatographically before determination.

H. F. W. KIRKPATRICK

2530. The absorption spectra of conjugated bile acids in sulphuric acid. S. Eriksson and J. Sjövall (Dept. Physiol. Chem., Univ. Lund, Sweden). *Ark. Kemi*, 1955, **8** (4), 311-315.—The absorption spectra of the common conjugated bile acids in various concn. of H_2SO_4 are described. As with the unconjugated acids, quant. determination was made with 65 per cent. H_2SO_4 . With the technique described earlier (*cf. Anal. Abstr.*, 1956, **3**, 2529), glycocholic, taurocholic, glycochenodeoxycholic and taurochenodeoxycholic acids were heated for 15 min. and glycodeoxycholic and taurodeoxycholic acids for 60 min. at 60° C. Measurements of cholic acid conjugates were made at 320 $m\mu$, of deoxycholic acid conjugates at 389 $m\mu$, and of chenodeoxycholic acid conjugates at 305 $m\mu$.

H. F. W. KIRKPATRICK

2531. New solvents for the separation of bile acids with paper chromatography. J. Sjövall (Dept. Physiol. Chem., Univ. Lund, Sweden). *Ark. Kemi*, 1955, **8** (4), 299-301.—With amyl acetate-heptane in various proportions as the mobile phase and 70 per cent. acetic acid as the stationary phase the R_F values of ten bile acids are tabulated. The use of amyl acetate is advantageous chiefly in the separation of bile acids conjugated with taurine, taurochenodeoxycholic and taurodeoxycholic acids being completely separated after 46 hr. by descending chromatography with amyl acetate-heptane (8:2). Mixtures of 1:2-dichloroethane and heptane as the mobile phase with 70 per cent. acetic acid as the stationary phase are especially suitable for separating bile acids for quant. determination with H_2SO_4 . Mixtures of 1:2-dichloroethane and *n*-butanol can be used for separating taurine conjugated acids.

H. F. W. KIRKPATRICK

2532. Quantitative determination of bile acids on paper chromatograms. J. Sjövall (Dept. Physiol. Chem., Univ. Lund, Sweden). *Ark. Kemi*, 1955, **8** (4), 317-323.—A procedure is described by which mixtures of bile acids are separated by paper chromatography, eluted and determined spectrophotometrically in 65 per cent. H_2SO_4 . With pure bile acids, singly or in mixtures, recoveries ranged from 96.5 to 102.5 per cent.

H. F. W. KIRKPATRICK

2533. The determination of higher fatty aldehydes in tissues. J. B. Wittenberg, S. R. Korey and F. H. Swenson (Sch. of Med., Western Reserve Univ., Cleveland, Ohio, U.S.A.). *J. Biol. Chem.*, 1956, **219** (1), 39-47.—A specific method is described for the determination of C_{14} or higher aliphatic aldehydes in tissue lipids. By reaction of the lipids with acid-*p*-nitrophenylhydrazine, the aldehydes are converted into their *p*-nitrophenylhydrazones, which are determined spectrophotometrically at 395 $m\mu$. The method, with an error of ± 5 per cent., will determine 0.1 to 7 μ moles of aldehyde. Lower aldehydes and keto acids do not interfere.

J. N. ASHLEY

2534. Determination of amino acids by ninhydrin oxidation and gas chromatography. Separation of leucine and isoleucine. I. R. Hunter, K. P. Dimick and J. W. Corse (U.S. Dept. Agric., Albany, Calif., U.S.A.). *Chem. & Ind.*, 1956, (16), 294-295.—The aldehydes liberated from the quantitative reaction of α -amino acids with ninhydrin are

removed from soln. with a stream of N and passed into a cold trap immersed in solid CO_2 -acetone or liquid N. They are then transferred to a second cold trap in series with the first and samples are removed for gas-liquid partition analysis. In this manner, samples of isobutyraldehyde, 3-methyl- and 2-methyl-butyraldehydes and acetaldehyde were prepared from valine, leucine, isoleucine and alanine, respectively. Details of the determination of leucine and isoleucine are given.

O. M. WHITTON

2535. Application of high-voltage electrophoresis combined with colour tests to the qualitative identification of amino acids in protein hydrolysates. G. A. Spengler and M. Knedel (Med. Poliklinik, Univ. Marburg, Germany). *Klin. Wochschr.*, 1956, **34** (13-14), 389-391.—The amino acids are separated by filter-paper electrophoresis, a potential of 5600 V for 50 min. and buffer soln. of pH 3.6 (pyridine-acetic acid-water) and pH 1.9 (acetic acid-formic acid) being used. Identification of the individual acids was made by means of various specific colour reactions in addition to the ninhydrin reaction. Tables are given showing the electrophoretic position and reactions of 18 amino acids.

H. F. W. KIRKPATRICK

2536. Control of the staining procedure after paper electrophoresis. C. Wunderly (Med. Univ. Clin., Zurich, Switzerland). *Nature*, 1956, **177**, 586.—The polyethyleneimine "Polymine" (mol. wt. 30,000 to 40,000) has been found to absorb Naphthalene black 12B as well as Sudan black, hence it can be employed for reference staining of both protein and lipoprotein. Application to paper strip, after electrophoresis but before staining, of a 0.05 per cent. aq. soln. of Polymine (0.02 ml) has resulted in greater uniformity and reproducibility of the stains. The solubility constants between dye, solvent and polybase have been found to be constant, and the Polymine standard may therefore be used as reference. Since the stain cannot be eluted, estimation by direct-reading colorimetry is necessary.

D. G. HIGGS

2537. Colorimetric determination of glutamic acid in protein hydrolysates. S. Kuk-Meiri and N. Lichtenstein (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1956, **14** (3), 266-268.—The glutamic and aspartic acids in protein hydrolysates can be adsorbed on Amberlite IR-4B columns (15 cm \times 1 cm, 40 to 60 mesh) at pH 3 to 4 and then eluted with N HCl. After concentration *in vacuo*, the eluate is treated with aq. NaNO_2 soln. and acetic acid to convert glutamic acid into the lactone of hydroxylglutaric acid, which is then converted into a hydroxamic acid by addition of 2 M hydroxylamine, according to the method of Sachs and Brand (*J. Amer. Chem. Soc.*, 1954, **76**, 3601). After addition of 0.37 M FeCl_3 soln. in 0.1 N HCl, the extinction of the hydroxamic acid-iron complex is immediately measured in a photoelectric colorimeter (filter No. 54). The values agree well with those obtained by the colorimetric method described previously (Zamir and Lichtenstein, *Anal. Abstr.*, 1955, **2**, 3440), even for 0.7 μ mole of glutamic acid in the sample.

W. J. BAKER

2538. Iodimetric estimation of tyrosine, tryptophan and methionine in mixtures of amino acids. L. Genevois and J. Baraud (Lab. Chim. Biol., Fac. Sci., Bordeaux, France). *Chim. Anal.*, 1956, **38** (3),

87-89.—The action, over a wide range of pH, of dil. soln. of I on various amino acids is described. Only tyrosine (I), tryptophan (II) and methionine (III) react below pH 6.0, and this forms the basis of a method for their determination in protein hydrolysates. *Procedure*—Eliminate cysteine if present by destruction with Na bromoacetate at pH 8.0. To a soln. of the sample containing \approx 3.5 mg of each acid (10 ml), add phosphate buffer soln. (pH 6.0) (10 ml) and 0.02 N I soln. (25 ml). I, II and III react, absorbing 4, 6 and 2 equiv., respectively, of I. Set the soln. aside for 2 hr. at 20° C, then titrate the excess of I with 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$ soln. Add HCl (2 ml) to bring the pH to 1.0, followed by an excess of $\text{Na}_2\text{S}_2\text{O}_3$ soln. (40 ml), and after 10 min. titrate the excess with standard I soln. Under these conditions 2 equiv. of I are liberated from the di-iodomethionine. To a second aliquot of the sample (10 ml) add acetate buffer soln. (pH 4.0) (10 ml) and 0.02 N I soln. (25 ml), and after 2 hr. titrate as before. Only II and III absorb I at pH 4.0. From the results obtained, calculate the amounts of I, II and III present.

D. G. FORBES

2539. Determination of arginine. J. W. Janus (Kodak Ltd., Wealdstone, England). *Nature*, 1956, **177**, 529.—The use of oxine in place of 1-naphthol for the determination of arginine and other monoalkyl guanidines by Macpherson's method (*Biochem. J.*, 1946, **40**, 470) results in a completely stable colour, a linear calibration graph and greater accuracy. The colour varies with temperature. The 7-chloro-oxine derivative gives greater sensitivity and lower blanks, and the additive colours due to other amino acids are only \approx 50 per cent. of the value found when oxine or 1-naphthol is used.

D. G. HIGGS

2540. Detection and determination of canavanine and arginine in biological materials. Saburo Muraoka and Yasushi Takagi (Pharm. Inst., Med. Fac., Kyoto Univ., Sakyo-ku). *J. Pharm. Soc. Japan*, 1954, **74** (12), 1341-1343.—Arginine (I) (isoelectric point, pH 10.8) and canavanine (II) (isoelectric point, pH 8.2) are separated by buffered chromatography (*cf.* Levy and Chung, *Anal. Chem.*, 1953, **25**, 396) with a phenol-borate buffer (pH 9.3), and show R_F values of 0.83 and 0.69, respectively. They can also be separated by paper electrophoresis with barbitone buffer (pH 8.6). Another effective separation is provided by the use of the ion-exchange resins Amberlite IRC-50 and IRA-400; I is adsorbed by the former resin from a soln. of pH 8.0 and II by the latter resin from 4 per cent. NaOH soln. Archibald's colorimetric determination of I (*J. Biol. Chem.*, 1946, **165**, 168) cannot be applied in the presence of II. Sakaguchi's colorimetric determination of II (*J. Biochem., Japan*, 1951, **38**, 91) is satisfactorily carried out in the presence of I, but vitiated by a reducing agent such as glucose. Microbiological determination with *Streptococcus faecalis* R provides only relative values.

K. SAITO

2541. Continuous zone electrophoresis by crossed velocity fields in a supporting medium. Analysis of protein fractions obtained from normal human serum. I. Brattsten (Inst. Biochem., Univ. Uppsala, Sweden). *Ark. Kemi*, 1955, **8** (4), 347-360.—The proteins of serum from a single donor were fractionated by continuous zone electrophoresis and the validity of the process was tested by submitting the fractions to other tests, namely,

nitrogen determination, u.v. absorption, conductivity determinations, and heterogeneity tests by electrophoresis and ultracentrifuging. Material from the principal maxima in the distribution curve was shown by paper electrophoresis to migrate as singular spots characteristic of γ -, β - and α -globulins and albumin. The α_2 -globulin fractions investigated contained at least four components. Protein distribution in the fractions can be obtained by measuring the extinction at 284 $m\mu$ and converting to nitrogen values by means of standard curves.

H. F. W. KIRKPATRICK

2542. Determination of 17-hydroxycorticoids in plasma. W. J. Reddy, N. A. Haydar, J. C. Laidlaw, A. E. Renold and G. W. Thorn (Harvard Med. School, Boston, Mass., U.S.A.). *J. Clin. Endocrin. and Metabolism*, 1956, **16** (3), 380-390.—A simple method is proposed for the determination of total (free and conjugated) 17-hydroxycorticosteroids in plasma. Blood samples are collected with heparin and the plasma is separated within 30 min. The plasma is mixed with 10 per cent. $ZnSO_4 \cdot 7H_2O$ and 0.5 N NaOH and centrifuged at 3000 r.p.m. for 30 min. The supernatant liquid is adjusted to pH 1 with H_2SO_4 and, after addition of Na_2SO_4 , is extracted with *n*-butanol. Two aliquots of the extract are evaporated to dryness on a water bath at 90° to 95° C; to one residue is added phenylhydrazine reagent (phenylhydrazine hydrochloride dissolved in 22 N H_2SO_4 , diluted with ethanol), and to the other 22 N H_2SO_4 diluted with ethanol. The resulting mixtures are heated on a water bath at 60° C for 20 min., then cooled in cold water for 3 min., and the extinctions are read at 410 $m\mu$, against blanks and standards. The recovery of conjugated steroids was 92 to 106 per cent. Results with normal subjects gave a range of 28 to 78 μg per 100 ml at 8.30 a.m. and of 15 to 19 μg per 100 ml at 5.00 p.m. In selecting control values it is essential to take this diurnal variation into account.

H. F. W. KIRKPATRICK

2543. Estimation of corticosteroids and their clinical significance. E. Diczfalussy, G. Birke and L.-O. Plantin (Karolinska Sjukhuset, Stockholm, Sweden). *Klin. Wochschr.*, 1956, **34** (9-10), 225-231.—The methods proposed for estimating steroids of the adrenal cortex in blood and urine are reviewed. The types of steroid estimated by particular reactions are tabulated, as are normal values found by various workers by means of these reactions. The methods and their chemical significance are discussed critically. (123 references.)

H. F. W. KIRKPATRICK

See also Abstracts 2450, 2502, 2503, 2580, 2581, 2587.

Drugs

2544. Recent advances in pharmaceutical analysis. Infra-red spectroscopy. T. Cånback (Apotekens Kontrollab., Stockholm, Sweden). *J. Pharm. Pharmacol.*, 1956, **8** (4), 225-231.—A brief review is given of some recent applications of i.r. spectroscopy to pharmaceutical problems, including the identification of unknown substances, tests of stability, and quant. measurements involving the isotope-dilution principle.

A. R. ROGERS

2545. A new approach to the assay of alkaloidal crude drugs. I. Cinchona and nuxvomica. E. Brochmann-Hanssen (Coll. of Pharmacy, Univ. California, San Francisco, U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (2), 74-77.—An

ion-exchange method is proposed for the extraction of the alkaloids of cinchona (I) or of nuxvomica (II); the alkaloids are then determined by u.v. spectrophotometry. The results are 10 to 15 per cent. higher than those obtained by conventional methods, and are more precise. It is shown that considerable loss of strychnine occurs during the oxidation of brucine in the U.S.P. assay of II. **Procedure**—Shake the finely powdered sample (0.1 g) with 2.5 N formic acid (1 ml), Dowex 50- X_2 (H^+ form) (1 g) and boiling H_2O (25 ml) for 30 min. (for I) or 15 min. (for II), maintaining a temp. of 80° to 90° C. Remove the crude drug residue by back-washing with H_2O . Wash the resin with 95 per cent. ethanol (25 ml), and elute the alkaloids with 4 N aq. NH_3 in 70 per cent. v/v methanol, passing the eluate through a column (15 cm \times 1 cm) of Dowex 1- X_1 (OH^- form). Collect the first 100 ml, and measure the extinction at 280 $m\mu$ and 332 $m\mu$ (for I), or 260 $m\mu$ and 304 $m\mu$ (for II), against a blank obtained by passing methanolic NH_3 soln. through the same anion-exchange column.

A. R. ROGERS

2546. Photometric determination of apomorphine hydrochloride. F. Machovičová (State Inst. for the Control of Drugs, Bratislava, Czechoslovakia). *Českosl. Farmac.*, 1956, **5** (1), 24-26.—Apomorphine is oxidised with $K_2Cr_2O_7$ and H_2O_2 in acetic acid. The coloured product formed is extracted with $CHCl_3$ and its extinction measured. Apomorphine hydrochloride (300 to 600 μg) can be determined in pharmaceutical preparations, and morphine hydrochloride does not interfere. K. A. PROCTOR

2547. A comparison of methods of assay of digitoxin tablets. W. A. Mannell, A. Lavalley, R. A. Carioto and M. G. Allmark (Food and Drug Lab., Dept. Nat. Health and Welfare, Ottawa, Canada). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (2), 98-101.—Comparative assays of 18 preparations of digitoxin tablets showed that the U.S.P. XV chemical method gave results lower than those by the U.S.P. XIV pigeon method. Better agreement could be obtained by analysing a chloroform eluate collected after the isolation of digitoxin, and estimating in addition the residual glycoside content (mainly gitoxin, which is also toxic to pigeons). Qual. analysis with paper chromatography showed that the U.S.P. XV method was an efficient means of isolating pure digitoxin.

A. R. ROGERS

2548. Photometric determination of adrenaline with potassium mercuric thiocyanate. É. Salgó, J. Kis and J. Morvay (Pharm.-Chem. Inst., Univ. of Szeged, Hungary). *Z. anal. Chem.*, 1956, **149** (5), 355-358.—The reaction of adrenaline (I) with $K_2Hg(SCN)_4$ (cf. *Brit. Abstr. C*, 1953, 316) gives a pink-red colour with an absorption max. at 500 $m\mu$ and a sensitivity of 2 μg per ml. The reaction appears to be specific for I and only large quantities of noradrenaline may interfere. A photometric method based on this reaction is accurate to within ± 3 per cent. for 50 to 300 μg of I. **Procedure**—Add 2 ml of 0.1 N $K_2Hg(SCN)_4$ to 5 ml of the freshly prepared soln. of I (2 to 3 mg per cent.) and make up to 10 ml. Keep at 100° C for 25 min., cool to room temp. and compare the extinction (2-cm cell, S50 filter) with that of a blank. Calculate the content of I from the calibration curve.

J. P. STERN

2549. The nature of the dose-response curve and its effect upon the error of the assay of vitamin B12. W. Weiss, H. Edelson and H. W. Loy (Food

and Drug Admin., Dept. Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (1), 167-172.—Sixteen samples of vitamin B₁₂ were analysed in duplicate by the U.S.P. method; results are presented in tabular form with relation to percentage potency, limits of potency and intervals between limits. The average length of the interval between the potency limits is 17 per cent. of the percentage potency when the points on the dose-response curve are joined by straight lines, 26 per cent. when they are joined by a smooth curve, and 33 per cent. when the best fitting straight line is drawn; thus the first of these procedures gives the most precise assay.

A. A. ELDRIDGE

2550. Colorimetric determination of santonins.

III. Discussion on the sodium methoxide method. Masaharu Yamagishi, Toshiko Yoshida and Hiroshi Fujiwara (Takeda Pharm. Ind. Ltd., Jusō-Nishinocho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1954, **74** (12), 1351-1353.—The authors' method for the determination of santonin (I) (*J. Pharm. Soc. Japan*, 1953, **73**, 875), which consists in the measurement of a red colour resulting from the interaction of Na methoxide (10 per cent. of Na in methanol, 2 ml) with I (> 1 mg per ml, 1 ml), was examined. The factor that gives greatest fluctuations is the variation in the Na methoxide soln. Atmospheric moisture appears to contribute in increasing the experimental error.

IV. Determination of santonin in *Artemisia kurramensis*, Quazilbash. Masaharu Yamagishi, Isao Nakamura and Kazuo Nakajima. *Ibid.*, 1954, **74** (12), 1354-1356.—A chromatographic separation of I in CHCl₃ soln. was studied with an alumina column. When the CHCl₃ is dry, I is partly adsorbed on alumina, in contrast to Fischer's result (*Arch. Pharm.*, 1943, **281**, 361). The use of CHCl₃ containing 1 per cent. of ethanol is recommended. The powdered sample (0.1 g) is heated with Ba(OH)₂ (0.2 g) and water (30 ml) in boiling water for 1 hr., filtered, and the residue is washed with water. The filtrate and washings are treated with 25 per cent. HCl (3 ml), heated for 30 min., cooled and extracted with CHCl₃ (4 portions of 5, 3, 2 and 2 ml). The CHCl₃ layer is passed through a column of alumina, over which a layer of anhydrous Na₂SO₄ and activated charcoal is placed. The alumina layer is washed with CHCl₃ (5 ml) and the CHCl₃ is evaporated to obtain pure I, which is submitted to colorimetry.

K. SAITO

2551. A polarographic determination of glycyrrhizic acid in *Succus liquiritiae*. H. Onrust, A. P. Jansen and B. S. J. Wöstmann (Netherlands Inst. of Nutrition, Amsterdam). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (11), 1515-1524.—The ground sample (1 g) is dissolved in boiling aq. dioxan (50 per cent. v/v) (30 ml), H₂SO₄ (3 per cent. v/v) (80 ml) is added and the soln. is heated under reflux for 3 hr. The soln. is cooled, then heated under reflux for 15 min. with chloroform (50 ml). The mixture is then continuously extracted with chloroform for 1.5 hr., and the chloroform layer is made up to 100 ml with chloroform. An aliquot (25 ml) is evaporated to dryness, the residue is dissolved in ethanol and the solution is made up to 25 ml. To a 3-ml portion are added ethanol (7 ml), 0.5 M acetate buffer (pH 5.0) (5 ml) and saturated KCl (1 ml) and the volume is made up to 25 ml with water. The clear soln. (20 ml) is transferred to a Novák electrode vessel and oxygen-free N is passed through at

0.25 litre per min. for 5 min. The glycyrrhetic acid is determined polarographically over a voltage range of -1.2 to -1.7 V vs. the S.C.E., and the glycyrrhizic acid is calculated from the result.

C. A. SLATER

2552. Chemical methods for the determination of antibiotics. I. Colorimetric determination of dihydrostreptomycin. Kiichiro Kakemi and Takaichi Arita (Pharm. Inst., Kyoto Univ., Yoshida-konocho, Sakyo-ku, Kyoto). *J. Pharm. Soc. Japan*, 1955, **75** (2), 192-194.—It was found that streptomycin and dihydrostreptomycin (I) react with sodium pentacyanoamminoferrate (II) and sodium hexacyanoferrate (III) in a basic soln. (pH 9.5) containing acetone (50 per cent.) to give an orange-red colour, which obeys Beer's law for 1 to 25 mg per 100 ml (730 units per mg). This method is used for a rapid assay of the sulphate of I in an ordinary injection. The potency obtained by this method is in good agreement with that obtained by the usual microbiological assay. The sample (1 ml) is treated with a buffer (pH 9.5, 1 ml), aq. soln. of II (0.05 M, 0.1 ml) and aq. soln. of III (0.025 M, 0.1 ml) and shaken well with acetone (2 ml). The extinction is measured at 500 mμ within 7 min. A similar method is applicable to other compounds containing a guanidyl group, such as sulphaguandine and arginine.

II. Colorimetric determination of oxytetracycline. Kiichiro Kakemi, Toyozo Uno and Masayoshi Samejima. *Ibid.*, 1955, **75** (2), 194-196.—It was found that oxytetracycline (IV) reacts with ammonium molybdate to give a red colour (max. absorption 500 mμ, no absorption at > 630 mμ), which obeys Beer's law at concn. < 50 μg per ml. When the sample contains a small amount of decomposition product, the extinction coefficients due to the latter are practically the same at 500 and 660 mμ. The sample (≈ 500 μg of IV per ml, 2 ml) is mixed with an acetate buffer (30 ml) and treated with ammonium molybdate in acetate buffer (pH 4) (1 per cent., 1 ml) at 60° C for 15 min. The product is extracted with a mixture of ether and ethyl acetate (1 + 1) (10 ml). The aq. layer is made up to 50 ml with the buffer soln. and the extinctions are measured at 500 and 660 mμ. The value obtained at 660 mμ is subtracted from that at 500 mμ and the amount of IV calculated.

K. SAITO

2553. Assay of possible carcinogenic hydrocarbons from cigarette smoke. M. J. Lyons (Royal Beatson Mem. Hosp., Glasgow). *Nature*, 1956, **177**, 630-631.—A total of 15 g of smoke products from the smoking of 500 cigarettes was collected at -70° C in acetone. A neutral aromatic fraction was subjected to chromatographic analysis on three different media, namely, silica gel, alumina and Florisil. Eluates and columns were observed under u.v. light and the eluates also by fluorescent spectrography. The findings of Cooper and Lindsey (*Brit. J. Cancer*, 1955, **9**, 304) were largely substantiated. Rechromatography of the 3:4-benzopyrene (I) fraction on alumina revealed the presence of two further compounds in low concn., which were more strongly held than I and showed a blue-violet fluorescence in the u.v. The fluorescent spectra of these two compounds were similar to that of I; one, however, showed a hypsochromic shift, with apparent increase of fine structure, and the other showed a bathochromic shift relative to I.

D. G. HIGGS

2554. **Qualitative and photometric determination of tetracaine [amethocaine].** O. Hrdý and A. Slouf (State Inst. for the Control of Drugs, Prague, Czechoslovakia). *Českosl. Farmac.*, 1956, **5** (1), 21-24.—A sensitive photometric method for the determination of 50 to 200 μ g of amethocaine is described. Interaction with an excess of Br produces a primary aromatic amine, which is then diazotised and coupled with N-1-naphthylethylenediamine to give an orange azo dye with max. extinction at 500 m μ . Neither adrenaline nor *p*-butylaminobenzoic acid interferes. A sensitive method for detecting amethocaine is based on the same reaction. K. A. PROCTOR

2555. **Qualitative and quantitative determination of diphenylpiperidinoethylacetamide methobromide; its detection in urine and faeces.** A. Häussler (Farbwerke Hoechst A.-G., Höchst, Germany). *Arzneimittel-Forsch.*, 1956, **6** (3), 142-145.—Diphenylpiperidinoethylacetamide methobromide (I) gives a red-violet colour with sodium diphenylaminoazobenzenesulphonate (Tropaeolin OO) (II), which may be used as the basis of a colorimetric assay. *Procedure*—Shake the soln. (0.1 to 50 ml containing 25 to 150 μ g of I) with an equal vol. of phosphate buffer (pH 7.3) and a 0.1 per cent. aq. soln. of II (3 ml). Extract with freshly distilled dichloromethane (4 \times 5 ml). Bulk the extracts, centrifuge, and to the organic phase add a 1 per cent. soln. of conc. H₂SO₄ in methanol (1 ml) and dilute with dichloromethane to 25 ml. Measure the extinction photo-electrically (5-cm cell, green filter). Urine samples are first shaken with Al₂O₃ and filtered; samples of faeces are extracted with 2 per cent. trichloroacetic acid in a Soxhlet apparatus, and the extract is assayed as described for urine. A. R. ROGERS

2556. **Colorimetric determination of 4-hydroxy-3-(1-phenylpropyl) coumarin.** J. Bednár (State Inst. for the Control of Drugs, Prague, Czechoslovakia). *Českosl. Farmac.*, 1956, **5** (1), 26-27.—4-Hydroxy-3-(1-phenylpropyl)coumarin (I) reacts with diazotised *p*-nitroaniline in Na acetate soln. to give a yellow product, which after oxidation is extractable with CHCl₃. The colour of the resulting soln. is measured. The method is applicable to the determination of I in tablets after extraction with Na acetate soln. K. A. PROCTOR

2557. **Volumetric determination of 3:4-dimethyl-5-sulphanilamidoisooxazole [sulphafurazole].** J. Blažek and Z. Stejskal (State Inst. for the Control of Drugs, Prague, Czechoslovakia). *Českosl. Farmac.*, 1956, **5** (1), 27-28.—Sulphafurazole (I) can be determined by titration with AgNO₃ in the presence of sodium borate. *Procedure*—To the injection soln. or tablets, containing about 400 mg of I in 50 ml of 55 per cent. ethanol, add 0.3 g of sodium borate and 40 ml of 0.1 N AgNO₃ and dilute to 100 ml with water. Filter and discard the first 20 ml of filtrate. To 25 ml of clear filtrate add 3 ml of HNO₃ and 3 ml of ferric ammonium sulphate soln. Titrate the excess of AgNO₃ with 0.1 N NH₄SCN. The method is stated to be accurate to within \pm 1.6 per cent. K. A. PROCTOR

2558. **Analysis of nitroglycerin tablets by infra-red spectrophotometry.** G. Schwartzman (Food and Drug Admin., Dept. Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off.*

Agric. Chem., 1956, **39** (1), 254-255.—A portion of powdered tablets containing about 50 mg of glycerol trinitrate is mixed with 15 ml of water and extracted with 20, 10 and 10 ml of CS₂. The filtered extract is diluted with CS₂ to 50 ml. A sample of 9 per cent. of glycerol trinitrate adsorbate on lactose containing about 50 mg is treated similarly. The recorded spectra of the sample and standard are compared from 2 to 15 μ to establish identity, and the baseline extinction of each is determined at 7.90 μ . A. A. ELDRIDGE

2559. **Experiences in toxicological analysis, particularly with the procedure of Feldstein and Klendshoj.** H. Pfeiffer and H. Diller (Chem. Invest. Inst., Nuremberg, Germany). *Z. anal. Chem.*, 1956, **149** (4), 264-269.—The toxicological analytical procedure of Feldstein and Klendshoj (*Analyst*, 1953, **78**, 43) and its modifications are discussed. Methods are given for tests for phosphorus-containing toxic insecticides and similar poisons (*e.g.*, tritoyl phosphate) and for the paper chromatography of inorganic constituents of organs (as used for the identification of metallic poisons). J. P. STERN

See also Abstracts 2387, 2423, 2455, 2502, 2507, 2564, 2565, 2566, 2572.

Food

2560. **Determination of glucose in invert-sugar solutions by hypiodite and the changes caused by heat treatment.** S. O. Eriksson. *Farm. Revy.*, 1955, **54**, 441-452, 456-461.—The literature of this method of analysis is fully reviewed. In present tests it was found that the use of \leq 30 ml of 0.1 N iodine soln. per 0.1 g of glucose (nearly three times the stoicheiometric requirement) is necessary for quant. results in 20 min. reaction time. The use of less Na₂CO₃ than employed by previous workers was then found desirable; amounts of 2.5 to 5 times the iodine, in molar proportions, are recommended. With larger amounts, especially if left in contact for a period before analysis, more fructose is oxidised. The use of smaller reaction volumes hastens fructose oxidation more than glucose oxidation; a volume of 100 to 150 ml appears best, so that for 0.1 g of glucose in 10 ml of soln., with 30 ml of 0.1 N iodine soln., 75 ml of 0.05 M Na₂CO₃ soln. should be added, with a reaction time of 20 min. at 23° C. Whilst the oxidation of fructose would be much less with 30 min. reaction time at 15° C, the rate of formation of iodate in the alkaline iodine soln. is much reduced by lower temperature and greater dilution. In the presence of the glucose, the rate of fructose oxidation is reduced, the oxidation of the fructose in invert sugar being equivalent, under the above conditions, to only 0.3 per cent. of the glucose. After reaction of the optimum amounts quoted above, the mixture is acidified with 10 ml of 5 N acid and excess iodine is titrated with 0.1 N Na₂S₂O₃. A blank determination should also be made. Some applications of the method to invert sugar used for infusions are described. Heating tests of very weakly acidified glucose, fructose, invert sugar or sucrose soln. for 1 to 3 hr. at 110° C showed that some degradation of fructose could occur, but that glucose was unaffected. The effects were followed by measurements of the specific rotations. The changes in the fructose (anhydride formation) increased the iodide consumption in subsequent analyses.

SUGAR IND. ABSTR.

2561. **Authentic packs of edible and inedible frozen eggs and their organoleptic, bacteriological and chemical examination.** H. A. Lepper, M. T. Bartram and F. Hillig (Food and Drug Admin., Dept. Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (1), 185-194.—The results of smell tests and of bacteriological counts are presented in tabular form together with the formic, acetic, lactic and succinic acid contents of the samples. The smell test is reliable when used by experienced examiners. For frozen eggs a bacterial count of over 5×10^6 per g with more than 7 mg per 100 g of formic, acetic or lactic acid indicates the presence of decomposed eggs. A. A. ELDRIDGE

2562. **Determination of added distinctive cations in whisky. I. Flame-photometric determination of strontium.** M. J. Pro and A. P. Mathers (Alcohol and Tobacco Tax Div. Lab., Internal Revenue Service, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (1), 225-235.—Traces of certain salts may be added to whisky as brand "labels." For the determination of Sr a 20-ml sample is evaporated to dryness and the residue heated to fuming with 2 ml of 60 to 70 per cent. HClO_4 and 1 ml of HNO_3 . After the addition of three further 0.5-ml quant. of HNO_3 and removal by evaporation of 75 per cent. of the HClO_4 , the soln. is transferred to a 10-ml flask containing 0.5 ml of 20 per cent. dextrose soln., 0.2 ml of a 0.1 per cent. H_3PO_4 soln. and 0.5 ml of a 0.2 per cent. H_2SO_4 soln. and diluted with H_2O . A standard soln. (2 p.p.m. of Sr, 20 p.p.m. of H_3PO_4 , 100 p.p.m. of H_2SO_4 , 1 per cent. of dextrose) is used to adjust the wavelength scale of the Beckman DU spectrophotometer to the point of max. emission (460.7 m μ) of the Sr line. The emission of the standard and the sample is read at this wavelength and the background of the respective soln. at 445 and 475 m μ . The effects on the Sr luminosity of various anions and cations that may be present have been studied and the results are tabulated.

II. Flame-photometric determination of lithium. M. J. Pro and A. P. Mathers. *Ibid.*, 1956, **39** (1), 236-241.—A 20-ml sample is evaporated to dryness and the residue heated to fuming with 2 ml of 60 to 70 per cent. HClO_4 and 1 ml of HNO_3 ; three 0.5-ml portions of HNO_3 are added at intervals and heating is continued until 75 per cent. of the HClO_4 is removed. The residue is diluted to 10 ml. A standard (2 p.p.m.) soln. of Li is used to adjust the wavelength scale of the Beckman DU spectrophotometer to the point of max. emission (670.8 m μ). The emission of the standard and the sample is read at this wavelength and the background of the respective soln. at 640 and 690 m μ . Lithium can be determined without band-width, continuum and radiation interferences from anions and cations likely to be present in whisky or used as markers. A. A. ELDRIDGE

2563. **Acidobutyrometric determination of fat in fat-producing yeasts.** J. Škoda and L. Šlechtová (Fak. potravn. technol., Vysoká škola chemicko-technol., Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (7), 1097.—To a mixture of H_2SO_4 (10 ml, d 1.810) and a suspension of fat-producing yeasts (11 ml), contained in a dairy butyrometer calibrated from 0 to 6 per cent., amyl alcohol (1 ml) is added, and the contents are well mixed and centrifuged. Readings are taken after the apparatus has been kept at 60° to 65° C for 5 min. The method is equally accurate and appreciably faster than the

extraction procedure of Kleinzeller and Škoda (*Chem. Listy*, 1950, **44**, 184). G. GLASER

2564. **The use of turbidity measurements in microbiological methods for vitamins.** H. W. Loy, jun., W. P. Parrish and S. S. Schiaffino (Div. Nutrition, Food and Drug Admin., Dept. Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (1), 172-179.—The response of *Streptococcus faecalis* to folic acid, of *Lactobacillus plantarum* to nicotinic acid and pantothenic acid, of *Lb. casei* to riboflavin and of *Lb. leichmannii* to vitamin B_{12} was measured turbidimetrically after incubation at $34 \pm 0.5^\circ \text{C}$ for 72 hr. and turbidimetrically after incubation for 18 hr. The curves show that the more rapid turbidimetric method is satisfactory provided that a correction is applied for the turbidity of the sample blank. A. A. ELDRIDGE

2565. **Application of the variable reference technique for the spectrophotometric determination of vitamins.** S. S. Schiaffino, H. W. Loy, jun., O. L. Kline and L. S. Harrow (Food and Drug Admin., Dept. Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (1), 180-185.—The variable reference technique permits the determination of several vitamins in the same soln. at the same time and with the same degree of accuracy as the usual methods afford. A twin-beam spectrophotometer is employed, the concentration of the reference soln. being varied to give the same extinction as the soln. being examined. Suitable spectral extinction curves were prepared for riboflavin, thiamine hydrochloride, nicotinic acid, nicotinamide, folic acid, pyridoxine hydrochloride, pyridoxal hydrochloride, pyridoxamine dihydrochloride and cyanocobalamin. A. A. ELDRIDGE

2566. **Further studies on the yeast method for vitamin B_6 .** W. P. Parrish, H. W. Loy, jun., and O. L. Kline (Div. of Nutrition, Food and Drug Admin., Dept. Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (1), 157-166.—Factors affecting the growth of *Saccharomyces carlsbergensis* in the presence of each of the three forms of vitamin B_6 have been studied. Optimum growth occurs in a medium of pH 3.5 to 4.5. Nitrogen can be supplied as $(\text{NH}_4)_2\text{HPO}_4$ or as ammonium sulphate, sulphamate, thiocyanate or acetate. Among the amino acids of casein hydrolysate essential for yeast growth are isoleucine, histidine, methionine, tryptophan and valine. Aspartic acid, glutamic acid, phenylalanine, threonine and tyrosine individually increase the growths but their elimination from a synthetic mixture produces no effect. In the presence of a high concentration of cystine, growth responses to pyridoxine and pyridoxal were equal, but that to pyridoxamine was less. A. A. ELDRIDGE

2567. **The analysis of minor components in food. I. Rapid spectrophotometric determination of ascorbic acid.** Hiroshi Imai and Tsuyoshi Fujitani (Food Ind. Exp. Sta., Hijiya-honmachi, Hiroshima). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (11), 1212-1215.—A rapid colorimetric determination of ascorbic acid (I) (10 to 200 mg per 100 g) with the sodium salt of 2:6-dichlorophenolindophenol (II) was studied. An amyl acetate extract of II has max. absorption at 525 m μ , the extinction of which remains unchanged for 4 hr. The sample is extracted with 2 per cent.

metaphosphoric acid and diluted to produce a 0.4 to 1.0 mg per cent. soln. of **I**. **II** soln. (5 ml in water) is added to the sample soln., which is rapidly extracted with amyl acetate for the extinction to be measured. Another 5-ml portion of the **II** soln. is added to metaphosphoric acid and similarly treated. The amount of **I** is determined from the difference in the extinction of the two extracts, which is proportional to the concn. of **I** up to 4 mg per 100 ml.

K. SAITO

See also Abstracts 2502, 2503, 2549, 2577.

Sanitation

2568. Methods for testing water used in industry. British Standards Institution (2 Park St., London). B.S. 2690:1956, 160 pp.—Comprehensive physical and chemical methods for the examination of water are given, and include specifications for testing water for steam generation already made in B.S. 1427. Many of the tests require good laboratory facilities and specialised knowledge, but several alternative methods are provided, and it is emphasised that an appropriate selection of tests is to be applied to each individual sample. Improved methods (e.g., for hardness, Ca and Mg, with EDTA; electrometric, absorptiometric, potentiometric, etc.), are introduced. In addition the following tests are specified; figures in parentheses indicate the no. of alternatives available—odour; total CO_2 (including carbonates); albuminoid NH_3 ; suspended solids (5); total solids; organic matter; tannins; chlorine demand; and determination of S^{2-} , NO_3^- , NO_2^- , Mn, Na, Zn, Pb, As (2), Cr and Hg. Appendices give procedures for the use of conductivity cells, for sampling for determination of the pH of condensates, and for sampling and addition of reagents for dissolved oxygen.

D. G. FORBES

2569. Continuous measurement of dissolved oxygen in water. H. S. Levine, W. V. Warren, E. C. Tsvoglou and W. W. Walker (U.S. Public Health Service, R.A. Taft Sanitary Engng Center, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (3), 343-349.—The principles are given for the design and operation of an instrument for the continuous measurement of dissolved oxygen in water, in which the oxygen content of a gas in equilibrium with the water is determined. The results are not influenced by temp., salt content, pollution, aeration constant, barometric pressure or the dissolved nitrogen content of the water.

J. H. WATON

2570. A mercurimetric method for determining chlorides in water. L. N. Lapin and R. Kh. Zamanov. *Gigiena i Sanit.*, 1954, (10), 16-19; *Ref. Zhur., Khim.*, 1955, (15), Abstr. No. 31,921.—To determine Cl^- in water, mix 10 ml of the water, 20 ml of ethanol (96 per cent.), 2 drops of a 1 per cent. soln. of diphenylcarbazone, and N HNO_3 dropwise till soln. is obtained. Titrate with 0.01 N $\text{Hg}(\text{NO}_3)_2$ to a violet-pink colour. For titrations > 1 to 1.5 ml use 0.1 N soln. Reproducibility of results is good even in analysis of drinking waters with low mineral content. The proposed method is simple, accurate, and convenient in lab. and field conditions.

C. D. KOPKIN

See also Abstract 2450.

Agriculture and Plant Biochemistry

2571. Methods of chemical analysis of trace elements in biological materials. VI. Analysis of

plant ashes by a polarographic method. 2. Katsuchi Yamamoto (Fac. Sci., Tohoku Univ., Katahira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (11), 1202-1205.—The polarographic reduction wave of Mn in the presence of Cu and Zn was studied in an NH_4Cl soln. containing tartaric acid, for application to the analysis of plant ashes. The presence of Fe^{2+} makes the wave of Mn indistinct. The sample (0.5 g) is dissolved in 6 N HCl (15 ml) and centrifuged. The residue is treated with aqua regia and then HCl and extracted with a very small amount of N HCl. Both HCl soln. are combined, treated with aq. bromine soln. to oxidise Fe^{2+} to Fe^{3+} and extracted 4 times with ether. The aq. layer is made up to 25 ml and a portion (1 to 2 ml) is treated with tartaric acid (30 per cent., 1.40 ml), NH_4Cl (20 per cent., 1.25 ml) and a sufficient amount of aq. NH_3 soln. to give a pH of 8.0 to 9.0. The polarogram of Cu ($E_{1/2}$, -0.32 V), Zn (-1.18 V) and Mn (-1.58 V) is recorded.

K. SAITO

2572. The analysis of commercial preparations of chlorophyll. II. M. Strell, A. Kalojanoff and F. Zuther (Tech. Hochschule, Munich, Germany). *Arzneimittel-Forsch.*, 1956, **6** (1), 8-11.—The analysis of further chlorophyll preparations has been carried out by the methods described in Part I (*Anal. Abstr.*, 1956, **3**, 2328). The copper preparations contain mainly isochlorin-*e*₄ and pyropheophorbide-*a* and their 2- α -hydroxyl derivatives; in one instance, small amounts of pheophorbide-*b* and pyropheophorbide-*b* were found. Analysis of an iron preparation yielded mainly purpurin 18 and rhodochlorin. Chlorin-*e*₆ and rhodin-*g*₇ were identified in preparations which were free from complex metals, together with purpurin 18 and rhodochlorin.

A. R. ROGERS

2573. Application of chromatography. XXI. Quantitative determination of ferulic acid in "Cruculon." Toru Masuda, Mitsuko Asai and Yoichi Sawa (Takeda Pharm. Ind. Ltd., Jusonishino-cho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1956, **74** (12), 1347-1350.—The colorimetric determination of ferulic acid (**I**), one of the active components of Cruculon (**II**) (a turmeric preparation), is greatly affected by vanillic acid (**III**), which is always present in **II** and extracted together with **I**. An effective separation of **I** and **III** is achieved by paper chromatography of a methanolic extract of **II** with 2.5 per cent. boric acid as developing agent. The spot of **I** is extracted with water and treated with diazotised sulphanilic acid in an ice bath. The resulting yellow colour is measured at 470 m μ . The extinction is proportional to concn. of **I** < 100 μg per 10 ml and remains unchanged for 1 hr. at room temp.

K. SAITO

2574. Comparison of the phasic and chromatographic methods for analysis of carotene in dehydrated alfalfa [lucerne]. R. A. Moffitt and J. W. Mehl (Dept. Biochem. and Nutrition, Univ. Southern Calif., Los Angeles, Calif., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (1), 255-259.—The phasic method for the determination of carotene (Baker *et al.*, *Ind. Eng. Chem., Anal.*, 1939, **11**, 104) gives higher results than the chromatographic method (Quackenbush, *J. Ass. Off. Agric. Chem.*, 1949, **32**, 480). The "carotene" soln. from the phasic method contains pigments which remain on a Supercel-MgO column when β -carotene is eluted with 13 per cent. acetone. These pigments, which

cause the higher values, are xanthophylls, zeaxanthin or similar pigments from fresh lucerne, and neo- β -carotene B and U from dehydrated lucerne.

A. A. ELDRIDGE

2575. New specific test for the insecticide "Bayer 17147" (Gusathion). O. Wollenberg and G. Schrader (Bayer A.-G., Wuppertal-Elberfeld, Germany). *Angew. Chem.*, 1956, **68** (1), 41.—A soln. of "Bayer 17147" (Gusathion, the dimethyl-dithiophosphoric acid ester of N-methylbenzaz-imide) (5 ml of a 0.005 per cent. soln. in 5 per cent. acetic acid) is heated with 1 ml of N-phenyl-1-naphthylamine (2 per cent. in acetic acid) and 2 ml of H_2O for 15 min. on a water bath at 50° to 60° C, then 2 ml of 2 N HCl are added and the heating is continued for 15 min. An intense blue-violet colour with an extinction max. at 570 $m\mu$ is formed.

C. A. SLATER

2576. Biological assay of endrin in leafy vegetables and its confirmation by paper chromatography. A. K. Klein, E. P. Laug, J. F. Tighe, L. L. Ramsey, L. C. Mitchell and F. M. Kunze (Food and Drug Admin., Dept. Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (1), 242-253.—The pesticides are extracted from the comminuted sample by light petroleum in the presence of water and Na_2SO_4 . Oily substances, which might form emulsions, are removed chromatographically with a mixture of Celite and MgO as adsorbent and light petroleum for elution. The eluate is then extracted with methyl cyanide saturated with light petroleum; the extract, diluted with water, is then extracted with light petroleum. The residue on evaporation of this extract is refluxed with 2 per cent. ethanolic KOH to decompose DDT, BHC, Methoxychlor, Parathion, and Malathion. Chlordane, Heptachlor and Toxaphene are thus partly degraded. The light-petroleum extract is then used for fly bioassay, the procedure for which is fully described. Endrin was thus evaluated at 0.1- and 0.5-p.p.m. levels with an accuracy of \approx 70 and 85 per cent., respectively. The presence of endrin may be verified by paper chromatography and by goldfish bioassay.

A. A. ELDRIDGE

See also Abstract 2559.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

2577. Rapid process for the determination of water in emulsions, ointments, pastes and viscous mixtures with the aid of a simple vacuum-drying apparatus and the "plane-weighing-glass" ("Planwägglas"). A. Purr (Inst. für Lebensmitt. Technol. und Verpackung, Munich, Germany). *Fette u. Seifen*, 1954, **56** (12), 1006-1010.—The "Planwägglas" (I), introduced by Heidbrink (*Fette u. Seifen*, 1951, **53**, 291), consists of two flat circular ground-glass plates (60 mm diameter), the top one of which can be raised and lowered by a suitable handle and hook. This weighing device is used in combination with a new, thermostatically controlled, vacuum-drying apparatus (described and illustrated) for gravimetric determinations of the water contents in liquid and semi-liquid mixtures (milk, butter, cheese, chocolate-spreads, jam, fruit-pulps, glues, etc.). The substance (\approx 100 mg) is placed on the lower glass plate of the dried and weighed I, immediately covered by the upper plate (to prevent evaporation), weighed, spread out into a film by raising the

upper plate with a rubbing motion and suspending it on the hooked handle. In this position the I is lowered into the heated vacuum-desiccator, over a suitable drying agent, and dried at 70° C at 10 to 12 mm pressure for 2 to 5 min. The final weighing of the dried substance is carried out with both glass plates close together to prevent water adsorption. The process, demonstrated on numerous examples, gives results accurate to within 0.15 per cent.

S.C.I. ABSTR.

2578. Continuous countercurrent adsorption or exchange process. J. A. Lewis (Peter Spence and Sons Ltd., Widnes, Lancs.). *Chem. & Ind.*, 1956, (16), 296-298.—A continuous countercurrent adsorption or exchange process, which is applicable on a large scale, is described. An adsorbent, eluent, and sample soln. are shaken together in bottle A and allowed to settle. The liquid is poured into bottle B which contains fresh adsorbent, and fresh eluent is poured into A. The bottles are again shaken. After settling, liquids are transferred from B to C (containing fresh adsorbent) and from A to B and fresh eluent is introduced into A. The series is extended until extraction is complete. Examples of successful separations include—Ni, Mn, Co, Cu and Fe as chlorides by using alumina as adsorbent and acetone containing 5 per cent. of HCl as eluent; nitrates of Fe and U by the use of cellulose powder with ether- HNO_3 as eluent; chlorides of Co and Cu in dilute HCl with "Basex" zeolite as adsorbent and H_2O as eluent; and the dyes diaminoazobenzene and Azorubin S with alumina and industrial alcohol. O. M. WHITTON

2579. A micro mixer-settler for laboratory continuous countercurrent solvent extraction. G. P. Wall (A.E.R.E., Harwell, Berks.). A.E.R.E. Rep. CE/R 1730, 25.7.55.—A micro mixer-settler giving a 100 per cent. stage efficiency with the systems studied has been developed. Two sizes are available, giving phase volume samples of 4 ml and 10 ml per stage, respectively. The sizes are interchangeable in one assembly and any number of assemblies can be linked together. The mixing-lift device is low-speed (350 r.p.m.) and each mixer can be individually adjusted for optimum performance. The system used was 20 per cent. of tributyl phosphate in odourless kerosene extracting uranyl nitrate from 0.25 M HNO_3 , the aq. phase containing initially 5 mg of U per g.

N. E.

2580. Aerosol chromatographic spray. G. Zweig (Charles F. Kettering Foundation, Yellow Springs, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (3), 428.—The use of aerosol bombs for spraying large paper chromatograms with ninhydrin dissolved in acetone or n-butanol is described. These aerosol bombs form a cheap, disposable and portable spray and obviate the necessity of cleaning, as found with other types of sprays when different reagents are being used.

K. A. PROCTOR

2581. Preservation of ninhydrin-amino acid chromatograms. G. Zweig (Charles F. Kettering Foundation, Yellow Springs, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (3), 428.—Ninhydrin-treated chromatograms can be preserved for months by dipping into dil. copper nitrate soln. (1 ml of saturated copper nitrate and 0.2 ml of 10 per cent. v/v HNO_3 , diluted to 100 ml with ethanol). After being rapidly neutralised with ammonia vapour and dried in air the papers are sprayed with a permanent crystal-clear acrylic spray.

K. A. PROCTOR

2582. Gas chromatography. Apparatus requirements for the quantitative application of gas-liquid partition chromatography. M. Dimbat, P. E. Porter and F. H. Stross (Shell Dev. Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 290-297.—Features of apparatus and methods for gas chromatography important in obtaining reproducible results are discussed. In quant. work the peak height has been shown to be virtually insensitive to flow rate but sensitive to temp. fluctuations, whilst the reverse is true of peak areas. To increase reproducibility a by-pass sample-injection system is suggested to eliminate the effects of sample-size variation and this obviates the necessity of calibrating with respect to sample size. An inert carrier material, firebrick, has advantages over Celite in ease of packing, lower pressure drop and better resolution, which makes it especially suitable for long columns. Coiled copper-tube columns (50 ft.) have been used in the separation of C_1 to C_6 hydrocarbons and C_8 to C_{10} paraffins. These columns are easily made and permit convenient thermal control. Thermal-conductivity detection is recommended for ease of construction, high sensitivity, stability and low time constant. Helium as the carrier gas has advantages in high sensitivity and low noise level.

K. A. PROCTOR

2583. A viscometer for dilute polymer solutions. A. W. Craig and D. A. Henderson (Polymer Corp., Ltd., Res. and Develop. Div. Sarnia, Ontario, Canada). *J. Polymer Sci.*, 1956, **19**, 215-218.—Equations are proposed for the kinetic-energy corrections as applied to each of the viscosity functions in common use with polymers, and a method of designing an Ubbelohde viscometer having negligible kinetic-energy correction based on the intrinsic velocity is suggested.

B. J. WALBY

2584. Sample collector for small volumes of gas. M. Kraus (Ústav org. chem., Čsl. akad. věd, Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (6), 929.—A sample collector for volumes of gas up to 500 ml, based on the principle of the Mariotte bottle, is described and illustrated. The device can also be used as a gas holder.

G. GLASER

2585. An improved apparatus for the determination of sulphur trioxide in gases. A. W. Fletcher (Fuel Res. Sta., Greenwich, England). *Chem. & Ind.*, 1956, (16), 303-304.—Corbett's method is used (cf. *J. Inst. Fuel*, 1951, **24**, 247), in which the gases are bubbled through a soln. of isopropyl alcohol in H_2O ; the H_2SO_4 mist is retained by means of a sintered-glass filter. The sulphate in the alcoholic soln. and in the washings from the filter is determined by a turbidimetric method. Advantages over Corbett's apparatus are claimed. The results of the two methods agree well.

O. M. WHITTON

2586. Removal of oxygen from solutions with the help of redox resins (electron exchangers). G. Manecke (Fritz-Haber-Inst., Max-Planck-Gesellschaft, Berlin-Dahlem, Germany). *Angew. Chem.*, 1955, **67** (19-20), 613-615.—A chemically stable redox resin is prepared by condensing quinol, phenol and formaldehyde; this will remove dissolved oxygen from water more quickly than the usual method with oxygen-free N_2 . The resin is suitable for laboratory use, but care should be taken to use

freshly regenerated material, and a suitable rate of flow must be chosen for the temp. employed.

J. H. WATON

See also Abstracts 2499, 2500, 2523, 2524, 2569.

Optical

2587. An automatic recording photometer. K. Marha and L. Jenšovský (Ústav hygieny práce, Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (6), 926-928.—A photometer, capable of automatically recording in short regular intervals the changes in intensity of 20 cells at elevated temp. over a period as long as 18 hr., is described. It has been designed for the purpose of following bacterial growth, as manifested by changes in turbidity, at blood-heat temp., but it can also be used whenever the kinetics of colour or turbidity reactions under constant conditions are to be followed.

G. GLASER

Thermal

2588. Convenient recording technique for rapid changes [of temperature]. A. D. Misener and C. Crowe (Univ. Western Ontario, London, Ontario, Canada). *Canad. J. Technol.*, 1956, **34** (1), 41-43.—The initial part (0 to 5 sec.) of the time-temp. curve, e.g., in transient heat-flow studies, can be obtained accurately by connecting the output (≈ 120 cycles) of the recorder amplifier to the vertical deflection plates of an oscilloscope and adjusting the sweep period (0.1 to 2 sec.) to cover the required time-interval, an external capacitance being used if necessary. At high ratios of sweep period to amplifier period a vertical trace traverses the face of the tube with a period equal to the sweep period and an amplitude proportional to the peak-to-peak voltage. The trace can be calibrated by pulsing the intensity of the oscilloscope beam with a multi-vibrator, and can be photographed with a Polaroid oscilloscope camera.

W. J. BAKER

2589. Apparatus for the determination of melting and boiling points. P. Sleightholm (Sci. Dept., Tech. Coll., Blackburn, Lancs.). *Chem. & Ind.*, 1956, (16), 300.—The apparatus gives very reliable and consistent results between 50° and 290° C. Medicinal paraffin can be used as the heating bath for temp. up to 240° C. and dibutyl phthalate up to 290° C. The heating liquid in a boiling-tube is stirred by means of a tube connected to a small teat, which is alternately pressed and released.

O. M. WHITTON

2590. A simple thermogravimetric balance. A. R. Vasudeva Murthy, D. S. Bharadwaj and R. M. Mallaya (Indian Inst. Sci., Bangalore, S. India). *Chem. & Ind.*, 1956, (16), 300-301.—The balance consists essentially of a McBain-Baker quartz-fibre spring balance (cf. *J. Amer. Chem. Soc.*, 1926, **48**, 690) calibrated before use. The sensitiveness of the springs ranges from 8 to 10 cm per g, the load usually being 0.1 to 0.3 g, and the elongation of the spring is measured with the travelling microscope and plotted against the temp. The temp.-loss in wt. curve for $Na_2HPO_4 \cdot 12H_2O$ is given and discussed. Results for this and for $MgSO_4 \cdot 7H_2O$, $BaCl_2 \cdot 2H_2O$ and $Na_2HPO_4 \cdot 2H_2O$ agree with those reported in the literature.

O. M. WHITTON

2591. Apparatus for differential thermal analysis. J. G. Brady, R. L. Eager and J. M. Humphrys

(Univ. Saskatchewan, Saskatoon, Canada). *Canad. J. Technol.*, 1956, **34** (1), 1-9.—In the apparatus described, the sample and inert standard are heated in a horizontal muffle-furnace (alundum tube). The cylindrical containers (0.5 in. \times 0.5 in.) are made of platinum foil (0.002 in. thick) and are connected to a 28-gauge chromel-alumel differential thermocouple. All temp. are recorded on a two-point strip-chart recorder, with a sensitivity shunt in the circuit. Good resolution of peak areas, with quant. results generally accurate to ± 15 per cent., were obtained in the rapid mineralogical analysis of fine clays and volcanic ash. W. J. BAKER

Electrical

2592. Polarographic apparatus. May & Baker Ltd., Dagenham, Essex (Inventor: H. A. Glastonbury). Brit. Pat. 745,904; Date Appl. 14.8.52.—The apparatus comprises a polarographic cell wherein the cyclic formation of drops constituting a renewable electrode is synchronised with a recurring potential sweep which is applied to the cell. Voltages proportional to the sweep voltage and to the resulting current are applied to a cathode-ray tube to obtain the required current-voltage curves or polarograms. The rate of drop formation is synchronised with the recurring potential sweep by means of a free-running multivibrator actuating a relay, which intermittently opens and closes a contact across a sweep condenser. The rate of drop formation is controlled by electrical influence on the interfacial surface tension of the material of the drops, e.g., the above-mentioned relay controls the charging of a pulse condenser to a predetermined voltage and the immediate discharge of this condenser into the electrode assembly at the end of the sweep in order to detach the drop and thus cause each drop to fall at a predetermined instant in the sweep cycle. J. M. JACOBS

2593. A new type of polarographic cell with a streaming mercury electrode. K. Györfi and L. Poós (Polytech. Univ. Budapest). *Magyar Kém. Foly.*, 1956, **62** (2), 64-66.—Details are given of a new, streaming mercury electrode, which is suitable both for ordinary and for oscillographic measurements. Its advantages are twofold. The area of the liquid-covered surface of the mercury stream, and also the separation of the electrodes, is constant. Also, on refilling the cell, the surface of the streaming mercury can be reproduced accurately, thus all measurements are directly comparable. A. G. PETO

2594. The flowing mercury electrode in polarography. I. V. S. Griffiths and W. J. Parker (Battersea Polytechnic, London). *Anal. Chim. Acta*, 1956, **14** (2), 194-200.—The cell is made of polyethylene and is cup-shaped. A polyethylene tube of 2-mm bore rises through the bottom of the cell; it is full of mercury, the meniscus coinciding with the open upper end. Within the tube is another tube of 0.5-mm bore which reaches to within 1.5 mm of the mercury meniscus. Mercury flows up the narrower tube, producing the desired flow at the meniscus, and down the annular space between the tubes. The means of producing and controlling the flow of Hg is also described. The mercury-pool anode is on the floor of the cell. The diffusion currents obtained are reproducible and free from maxima. Wave heights are proportional to the concn. of the reducible ion. W. C. JOHNSON

2595. A simple dip-type saturated calomel electrode for polarography. P. O. Kane (May and Baker, Ltd., Dagenham, England). *Chem. & Ind.*, 1956, (16), 295-296.—The electrode chamber has a hole communicating with the salt bridge. A film of saturated KCl between the conical base of the salt bridge and an ungreaed sleeve connects the salt bridge to the polarographic cell soln. by means of a hole in the cone. A coating of paraffin wax at the top of the electrode vessel and salt bridge minimises creep of KCl. The electrode does not appreciably contaminate the soln. under investigation, has a reproducible potential, and may be readily cleaned and refilled. Polarisation by anodic currents up to 20 micro-amp. has been found to be 2 mV and at 50 micro-amp. only 9 mV. The electrode, however, has a resistance of 3000 ohms, necessitating appreciable corrections for ohmic potential. O. M. WHITTON

2596. Inverse polarography with stationary amalgam electrodes. I. Basic principles and technique. A. Hickling, J. Maxwell and J. V. Shennan (Liverpool Univ., England). *Anal. Chim. Acta*, 1956, **14** (3), 287-295.—Inverse polarography is a new electrochemical method for extracting certain heavy metals (Zn, Cd, Tl, Pb, Cu, Mn) from aq. soln. (1 ml), when present in small amounts and dilutions $< 0.1 M$, by quant. discharge into a mercury cathode (1 sq. cm). The amalgam electrode is then washed and combined with a standard reference electrode (Hg in contact with excess of $HgSO_4$ in saturated aq. K_2SO_4 or KNO_3) and the resulting cell is allowed to supply a current (I) against an opposing voltage (V) set up on a potentiometer. By decreasing V in stages, a curve of I vs. potential can be constructed for the anodic dissolution of the amalgam, each metal having a well-defined characteristic wave, from the height of which the concn. of any metal in the amalgam can be calculated. The apparatus, circuit and operation are described fully, and typical anodic dissolution curves for different metals are shown. Provided that calibration curves for different concn. of metal ion are obtained, an unknown amount of metal $> \approx 10^{-6}$ equiv.-wt. can be determined to within ± 1 per cent. The sensitivity is greater than in the conventional polarographic procedure, and the method is sometimes simpler. W. J. BAKER

2597. Studies on polarographic analysis. XX. The Ishibashi-Fujinaga differential polarograph. (Part 3.) Taitiro Fujinaga (Dept. of Chem., Fac. Sci., Kyoto Univ., Sakyo-ku, Kyoto). *J. Electrochem. Soc. Japan*, 1955, **23** (10), 537-540.—The instrument (Ishibashi and Fujinaga, *Bull. Chem. Soc. Japan*, 1950, **23**, 261) was slightly modified to increase the mechanical strength. The coincidence between the peak potential and the half-wave potential is mathematically explained for a reversible polarogram. The relation between the peak current and the differential voltage is discussed for zinc and cadmium ions in an ammoniacal and in a KCl soln. The limit of determination of traces of Zn (which is reduced at a more negative potential), in the presence of a large amount of Cu and Cd, is discussed. The compensation of the former wave is so satisfactorily achieved with this instrument that 0.1 per cent. of Zn in Cu or Cd can be determined in 0.1 N H_2SO_4 (for Cu) or in an ammoniacal soln. (for Cd).

XXI. The Ishibashi - Fujinaga differential polarograph. (Part 4.) Taitiro Fujinaga. *Ibid.*, 1955, **23** (11), 588-590.—The peak current of a reducible ion is so independent of the co-solute in the regulating soln. that it directly indicates the concn. of the ion. A direct-reading concn. meter was designed by the use of a potentiometer, a galvanometer and the differentiator. Its use for the determination of Zn (> 0.75 millimole per litre) ($E_1 = -1.4$ V vs. the S.C.E.) in the presence of Cu and Cd (< 10 times the weight of the Zn) was studied in M aq. $\text{NH}_3 - \text{NH}_4\text{Cl}$ soln. The presence of Ni (> 0.001 mole per litre) vitiates the determination of Zn. This method appears to be suitable for the rapid determination of Zn in brass. K. SAITO

2598. Acid-base titrations with a tellurium electrode. A. R. Tourky, I. M. Issa and S. A. Awad. *Chim. Anal.*, 1955, **37** (11), 367-371.—Three types of tellurium electrodes are studied. Electrodes of pure tellurium rod or made by electrolytic deposition of Te from a weakly acid soln. (10^{-3} N HCl) of TeO_2 give linear portions of the potential vs. pH curve between pH 1 and 5 and between pH 7 and 12. An electrode made by depositing Te electrolytically from a more strongly acidic soln. (1.5 N HCl) of TeO_2 gives a linear portion of the potential vs. pH curve over the range pH 3 to 12. Such an electrode is suitable for measuring pH in this region and for detecting the end-points of acid-base titrations. Values of pK'_a are given for several dibasic acids. J. H. WATON

2599. Amperometric titrations of micromolar solutions. J. G. Nikelly and W. D. Cooke (Cornell Univ., Ithaca, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 243-245.—An apparatus and procedure for making amperometric titrations of very dil. soln. (10^{-5} to 10^{-7} M) of Cd, Cu, Pb, Ni and Zn with EDTA (disodium salt), with a mercury-pool indicator electrode, are described. The electrode area is const. at 1 to 2 sq. cm and stirring is effected by bubbling N through the soln. The standard soln. should be ≈ 100 times the concn. of the ion being titrated, whilst supporting electrolytes should be such that the E_1 values of the ions being titrated are as positive as possible. The mean error is within ± 1.5 per cent., depending on concn. and nature of ion. Solutions containing $0.02 \mu\text{g}$ of Cd per ml can be titrated with a mean error of $0.0001 \mu\text{g}$. Titrations of Ni and Zn should not be made at dilutions $> 10^{-6}$ M. W. J. BAKER

2600. Polarographic cell assembly for amperometric titrations. J. P. E. Human and S. J. Leach (Biochem. Unit, Wool Textile Res. Lab., C.S.I.R.O., Melbourne, Australia). *Chem. & Ind.*, 1956, (9), 149-150.—Full details are given of a cell designed for amperometric titrations in conjunction with a Tinsley Polarograph Type 15 S. A modified side-arm with an orifice allows additions of reagents to be made by insertion of a burette, as well as the use of a stream of N to remove air from the soln. in the main part of the cell. Provision is also made for an external as well as internal reference electrode. H. F. W. KIRKPATRICK

2601. pH Meters. G. Girault-Vexlearschi. *Chim. Anal.*, 1955, **37** (11), 375-383.—After a brief review of types of electrodes, various types of pH meters are described, which are classified as "null position" and "direct reading" instruments. Among the

examples described in the second group are instruments in which a negative feed-back and a moving condenser are used. Apparatus for continuous recording and automatic control is mentioned, as well as two recent French electrostatic pH meters. J. H. WATON

2602. Application of high-frequency methods to detection of bands in partition chromatography. F. Baumann and W. J. Blaedel (Univ. Wisconsin, Madison, Wis., U.S.A.). *Anal. Chem.*, 1956, **28** (1), 2-4.—Where conductance or capacitance changes occur in the eluent from partition chromatography, high-frequency detection has advantages over the low-frequency methods in that external electrodes may be used. To follow the separation of carboxylic acids, a 4-Mc. tuned-grid, tuned-anode oscillator was used and changes in grid voltage during the elution of the acids were measured. The apparatus used for the detection is essentially that of Hall (*Anal. Chem.*, 1952, **24**, 1244). The record takes the form of deflections (V) against volume of eluate (ml) collected. D. G. HIGGS

2603. A collimated windowless Geiger counter for scanning chromatograms. D. R. Bangham (Nat. Inst. for Med. Res., Mill Hill, London). *Biochem. J.*, 1956, **62** (4), 550-551.—A simple windowless He-ethanol counter is described. It operates in the Geiger region with a standard rate meter. It is designed to give narrow collimation and a low background suitable for scanning paper chromatograms or paper-electrophoresis strips. J. N. ASHLEY

2604. A simple helium-ethanol flow counter for monitoring chromatograph-column effluents containing weak β -emitting isotopes. D. R. Bangham (Nat. Inst. for Med. Res., Mill Hill, London). *Biochem. J.*, 1956, **62** (4), 552-553.—The flow counter described is suitable for indicating the radioactivity due to weak β -emitting isotopes, such as ^{14}C or ^{35}S , in the eluate from a chromatographic column. It provides a continuous, immediately available record of radioactivity coming off a column, and eliminates many tedious sampling operations. It is not intended to be an accurate measuring instrument. J. N. ASHLEY

2605. Analysis of substances by measurement of nuclear magnetic relaxation times. Schlumberger Well Surveying Corp. (Houston, U.S.A.). Brit. Pat. 745,873; Date Appl. 13.1.54.—The technique is based on the fact that the nuclei of certain atoms precess when exposed to a magnetic field. Different substances, containing a common element (e.g., hydrogen) are distinguished by measuring their respective relaxation times. The substance is exposed simultaneously to a strong, homogeneous magnetic field of constant intensity and to a magnetic field alternating at the nuclear precession (harmor) frequency. Means are provided for obtaining indications of the energy absorbed from the high-frequency field as a result of nuclear resonance phenomena, e.g., either the frequency of the alternating field or the strength of the constant field is modulated over a portion of the resonance line-width. The apparatus is mainly intended for investigating substances in bore-holes and distinguishing oil from water reservoirs in earth strata. J. M. JACOBS

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current	a.c.	millicurie	mC
ampere	amp.	milligram	mg
Angstrom unit	Å	millilitre	ml
anhydrous	anhyd.	millimetre	mm
approximate, -ly	approx.	millimicron	mμ
aqueous	aq.	millivolt	mV
atmospher, -e, -ic	atm.	minimum	min.
boiling-point	b.p.	minute (time)	min.
British thermal unit	B.Th.U.	molar (concentration)	M
calorie (large)	kg-cal.	molecul -e, -ar	mol.
calorie (small)	g-cal.	normal (concentration)	N
centimetre	cm	number	no.
coefficient	coeff.	observed	(obs.)
concentrated	conc.	ounce	oz
concentration	concn.	part	pt.
critical	crit.	patent	pat.
crystalline	} cryst.	parts per million	p.p.m.
crystallised		per cent. wt. in wt.	per cent. w/w
cubic	cu.	per cent. wt. in vol.	per cent. w/v
current density	c.d.	per cent. vol. in vol.	per cent. v/v
cycles per second	c.p.s.	potential difference	p.d.
decompos -ing, -ition	(decomp.)	pound	lb
density	ρ	precipitate	ppt.
density, relative	d or wt. per ml	precipitated	pptd.
derivative	deriv.	precipitating	pptg.
dilute	dil.	precipitation	pptn.
direct current	d.c.	preparation	prep.
distilled	dist.	qualitative, -ly	qual.
electromotive force	e.m.f.	quantitative, -ly	quant.
electron-volt	eV	recrystallised	recryst.
equivalent	equiv.	refractive index	n _D
experiment	expt.	relative humidity	R.H.
foot, feet	ft.	revolutions per minute	r.p.m.
gram	g	saponification value	sap. val.
gram-molecule	mole	saturated calomel electrode	S.C.E.
half-wave potential	E _{1/2}	second (time)	sec.
horse-power	h.p.	soluble	sol.
hour	hr.	solution	soln.
hydrogen ion concentration	[H ⁺]	specific gravity	sp. gr.
hydrogen ion exponent	pH	specific rotation	[α] _D
inch	in.	square centimetre	sq. cm
infra-red	i.r.	standard temperature and pressure	s.t.p.
insoluble	insol.	temperature	temp.
kilogram	kg	ultra-violet	u.v.
kilovolt	kV	vapour density	v.d.
kilowatt	kW	vapour pressure	v.p.
maxim -um, -a	max.	volt	V
melting-point	m.p.	volume	vol.
microcurie	μC	watt	W
microgram	μg	wavelength	λ
microlitre	μl	weight	wt.
micron	μ		
milliampere	mA		

In addition the following symbols are used—

greater than	>	less than	<
not greater than	≧	not less than	≦
is proportional to	∝	of the order of, approximately	≈

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicles are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, e.g., Cu⁺⁺, Al⁺⁺⁺, Cl⁻, SO₄⁻². Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, e.g., ferric iron becomes Fe^{III} and cuprous copper Cu^I.

ANALYTICAL ABSTRACTS

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